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Notice

This volume is the fourth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with non-ferrous metals and includes papers presented at the Cleveland Meeting, Sept. 9–12, 1929, and the New York Meeting, Feb. 17–20, 1930.

The series is a continuation of the previous publications and proceedings of the Institute of Metals Division. The complete list of publications and proceedings, including the present volume, is as follows:

1908–1911 *Transactions* of the American Brass Founders' Association.

1912–1916 *Transactions* of the American Institute of Metals.

1917 *Journal* of the American Institute of Metals.

1918–1926 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 69, 70, 71 and 73.

1927 PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

1928 PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

1929 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Institute of Metals Division.

1930 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Institute of Metals Division.

CONTENTS

Melting and Casting Metals

Properties of Metals

X-ray Investigations

System Cadmium-mercury

FOREWORD

This is the fourth separate volume of the proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. The contents represent a fine balance between science and application. Also, the diversity of subjects is large for a single volume. The high quality of the authorship of the papers will be apparent to one familiar with non-ferrous metals. A number of the papers came unsolicited but the Papers Committee, under the chairmanship of Sam Tour, has to a large extent secured such papers as were desired to constitute symposia which lend a measure of continuity to the several volumes. In accordance with this plan, these volumes, during a period of years, should cover practically every important non-ferrous metal and the many processes to which metals and alloys are subjected during fabrication.

It is interesting to note that much of the new metal art of today can be traced to the metal science of yesterday. This represents a reversal of the older and almost universal order of art preceding science. By referring to the metal science presented in the 1927 volume of the Institute of Metals Division and the art as reflected in the present volume, the order of science preceding art can be seen clearly. This represents one of the greatest contributions of the Division; in fact, one of the greatest services the Division can render to the metal industry.

Valuable as are these volumes of TRANSACTIONS, they make no attempt to "bring forward" as a part of a new volume the most valuable portions of previous volumes. Each volume is a permanent record of the contributions made during the year. To meet the desire for up-to-date information including that which is not necessarily new, the Data Sheet Committee, under the chairmanship of R. S. Archer, was established in 1927. The Institute of Metals Division established working relations with the American Society for Steel Treating, which agreed to publish the Non-ferrous Metals Data Sheets prepared under the auspices of the Data Sheet Committee and to send the printed sheets to the members of the Institute of Metals Division. These data sheets are also published in bound form by the American Society for Steel Treating in the National Metals Handbook. The 1930 edition of the handbook contains 218 pages of non-ferrous data sheet material. New data sheets are in process of preparation and each edition of the handbook should contain additional non-ferrous material.

ZAY JEFFRIES, *Chairman,*
Institute of Metals Division

5

A. I. M. E. Officers and Directors

For the year ending February, 1931

6

SAMUEL L. HOYT

Institute of Metals Division Lecturer, 1930

Hard Metal Carbides and Cemented Tungsten Carbide

By Samuel L. Hoyt,* Schenectady, N. Y.

Cemented tungsten carbide, a product of a branch of metallurgy which has never possessed more than a relatively minor interest and importance, has recently commanded the attention of engineers, industrialists, financiers and men of business. New methods, new opportunities, new goals, never before considered, have suddenly been brought within the scope of practical realization. It is these results that attract the interest of the world, but we, as engineers and metallurgists, will have equal interest in the product itself and in that branch of metallurgy from which it comes. It seems appropriate, therefore, to speak today on Hard Metal Carbides and Cemented Tungsten Carbide, as the latter represents one of the outstanding developments of recent date in nonferrous metallurgy.

We are interested in the hard metal carbides as a group of related metallic substances and in cemented tungsten carbide as the leading representative of the metallurgy of this group. The literature of this general field is limited, and, bearing this in mind, it seems advisable to attempt to cover the field broadly and to correlate the subject matter, rather than to present a detailed account of any one of its phases. Our annual lecture lends itself admirably to this plan.

The quickened interest in cemented tungsten carbide, once its potentialities were recognized, the many sides to the problem of developing the manufacture and use of this new product, and the desire to economize as much as possible in the time of development, have brought many into this work, both in this country and abroad, notably the Osram Lamp Co. and Friedrich Krupp in Germany and the General Electric Co. in this country. It would be presuming too much to attempt to speak too broadly of the present state of the art and science of the hard metal carbides and my remarks are guided largely by the work done in the General Electric Co., and by our associates in the Carboloy Co. Even here the activities of many in these two groups have centered around the utilization of cemented tungsten carbide, which is outside the scope of this talk. To those whose work is represented in this lecture, it is my pleasant duty to acknowledge their assistance and advice. To Dr. Zay

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Jeffries and Mr. W. P. Sykes, of the Incandescent Lamp Department and to Dr. T. A. Wilson, Dr. Saul Dushman, Mr. T. S. Fuller, Mr. L. L. Wyman, Mr. F. C. Kelley, Dr. Dorothy Hall Brophy and Mr. R. Palmer, of the staff of the Research Laboratory, and to my assistants Mr. A. J. Carruthers, Mr. H. C. Staehle, Mr. M. C. Fetzer, Mr. W. J. Rothemich and Mr. T. R. Schermerhorn, now deceased, I am particularly indebted. I also wish to express my appreciation to Dr. George K. Burgess and Dr. H. S. Rawdon of our national Bureau of Standards for their particularly welcome assistance in determining various properties of cemented tungsten carbide and their permission to include these findings here. Finally, I am indebted to Dr. W. R. Whitney and Mr. L. A. Hawkins, of the Research Laboratory, under whose direction this work has been done, for their interest and support, and to the officials of the General Electric Co. for their consent to publish the material of this lecture.

Before passing on, may I take this opportunity to congratulate Messrs. Karl Schroeter and Heinrich Baumhauer of the Osram Lamp Co. Berlin,, on their splendid achievement in showing us how to utilize the superior hardness of tungsten carbide by their pioneer work on cemented tungsten carbide.

HARD METAL CARBIDES

Carbon combines with many of the elements. Most of these combinations are of but occasional interest in metallurgy and will not be considered here. This also applies to the carbides of calcium, aluminum, etc., which decompose in water or moist air, and to the carbides of boron and silicon, which are non-metallic and are of particular interest as refractories and abrasives. The carbides which I propose to discuss are those of the elements of the periodic system in the columns headed by titanium, vanadium and chromium, which form a group of "hard metal carbides." This group of carbides has long attracted the attention of those who are interested in the uses and applications of hard materials.

Curiously enough, these elements form a group in the periodic table which contrasts in atomic arrangement and in properties with the group whose metallic character is more pronounced and which is headed by the elements copper, iron, cobalt and nickel. With the elements of the latter group, carbon has little affinity except for its well-known behavior with iron, cobalt and nickel.

In the latter part of the preceding century attention was called to electric-furnace products and to certain carbides which have since become of industrial importance. Among the pioneers in this field may be mentioned Troost and Hautefeuille, Siemens and Huntington, Acheson, Riche, and, of course, Henri Moissan, who has brought all of this early work together in his classical treatise, "The Electric Furnace." Moissan

reported on methods of preparation, chemical composition, physical properties and chemical behavior of the following carbides: Cr_3C_2, Cr_4C, Mo_2C, W_2C, U_2C_3, VC, ZrC, TiC and ThC_2. Several were found that were hard enough to scratch quartz and some that would scratch corundum.[1]

With the development of the technique of carrying out metallographic investigations, some of the carbide systems have since been studied systematically, notably by Ruff and his collaborators, and more recently by Japanese investigators. Lately the metallic carbides have been studied by the methods of X-ray crystal analysis, principally by German and Swedish investigators, and this work gives us not only the atomic arrangement of these carbides but also provides a powerful tool for the study

GROUP 4		GROUP 5		GROUP 6	
Metal	*Carbide*	*Metal*	*Carbide*	*Metal*	*Carbide*
Ti-HCP d=2.92 c=4.67	Ti C-FCC	V-BCC d=3.04	V₆ C-Hex VC-FCC	Cr-BCC d=2.875	Cr₄C-FCC Cr₇C₃-Hex. Cr₃C₂-Orth
Zr-HCP d=3.23 c=5.14	Zr C-FCC	Nb-?	Nb C-FCC	Mo-BCC d=3.143	Mo₂C-HCP ?-HCP
Hf-HCP d=3.92 c=5.46	?	Ta-BCC d=3.272	Ta C-FCC	W-BCC d=3.155	W₂C-HCP WC-Hex
Th-FCC d=5.04	ThC₂-?	Pd-?	?	U-? not cubic	U₂C₃-? ?

FIG 1.—ATOMIC ARRANGEMENT OF THE HARD METAL CARBIDES.
Lattice parameters are in Ångström units, and are those reported in the International Critical Tables. Symbols represent arrangement of metal atoms, as follows:
FCC, face-centered cubic   *Hex*, hexagonal
BCC, body-centered cubic   *Orth*, orthorhombic
HCP, hexagonal close-packed

of the constitution of the systems. The next step in the general study of the metallic carbides will be a closer study of binary and higher order systems of the carbides among themselves and with other elements. The work that has been done on the various alloy steels will serve as a starting point for such studies.

With the purposes of the present presentation in mind, the literature of the hard metal carbides is not extensive and leaves many points unsettled and even untouched. It deals mainly with methods of preparing the carbides, physical and chemical properties of the carbides produced, phasial or constitutional relationships in the metal-carbon systems,

[1] H. Moissan: The Electric Furnace. Easton, Pa., 1904. Chemical Publishing Co.

and with X-ray data. For convenience, the periodic arrangement of these elements, showing the carbides which each forms, is given in Fig. 1,

PERIODIC ARRANGEMENT OF ELEMENTS OF HARD METAL CARBIDES

Titanium and zirconium apparently are very similar in behavior towards carbon, for each one forms a monocarbide and we have TiC and ZrC. Both of these carbides scratch quartz and ruby and the titanium carbide has been reported as hard enough to scratch corundum. A second carbide of zirconium, ZrC₂, was reported by Troost,[2] and was said to be harder than glass. Hafnium has not been reported on, but we would expect that element to behave somewhat like zirconium. Thorium forms a carbide, ThC₂, which decomposes in water, and little attention has been paid to it in connection with hard metal carbides.[3]

Beginning with the next series, vanadium forms VC, which resembles the titanium carbide in some respects. Osawa and Oya[4] report V₅C and V₄C₃, which form two eutectiferous series from vanadium to the higher carbide. The first carbide, V₅C, is given as hexagonal with an axial ratio of 1/6, and the second as having a face-centered cubic arrangement of the metal atoms. In a general report on the atomic arrangement of some of the common carbides, Becker and Ebert report that TiC, VC, ZrC, NbC and TaC all have the face-centered cubic arrangement of the metal atoms.[5] Obviously this does not agree with the report of Osawa and Oya that V₄C₃ forms, and in the recapitulation in Table 2 I have taken the liberty of reporting the V₄C₃ as VC.

Columbium, or niobium, forms the carbide NbC. This carbide has not been reported on to any extent, but it is probably similar to the tantalum carbide, TaC. Both of these carbides are characterized by having extremely high melting points, as is shown in Table 2, and both are known to be hard. The element protactinium at 91 is an extremely rare radioactive element and need not be considered here.

Chromium Carbides

Chromium heads the next column in the periodic table, and is known to form several carbides. With the possible exception of Cr₃C₂ there is considerable uncertainty as to the composition of the chromium carbides, although X-ray analysis shows that at least three such carbides form. The uncertainty is largely that of stating the formulas corresponding to the phases which have been found. Moissan gives Cr₄C as the first,

[2] L. Troost: Sur la préparation du zirconium et du thorium. *Compt. rend.* (1893) **116**, 1227.

[3] H. Moissan: *Op. cit.*

[4] A. Osawa and M. Oya: An Investigation of the Vanadium-Carbon System. *Kinzoku no Kenkyu* (1928) **5**, 434.

[5] K. Becker and F. Ebert: The Crystal Structure of Some Binary Carbides and Nitrides. *Ztsch. f. Phys.* (1928) **31**, 268.

pr chromium-rich, carbide, with a density of 6.75, which is concurred in by Westgren and Phragmén.[6] Ruff,[7] and Ruff and Foehr,[8] in greater detail, report on the most extended investigation of the chromium-carbon system that has been made. They gave this carbide as Cr_5C_2. Nischk has pointed out that compositions up to about 11 per cent. C were found to have duplex structures under the microscope and, accordingly, the first carbide to form was said to be more likely of the composition Cr_2C.[9] Ruff[10] criticized the etching reagent used by Nischk as being insufficient to develop the true structures of the chromium carbides and still maintained that the first carbide to form was the Cr_5C_2.

Except for the carbide Cr_3C_2, there is also considerable uncertainty as to the identity of the higher carbides. According to Ruff and Foehr the first carbide forms a eutectiferous series with chromium, while above Cr_5C_2 the carbides Cr_4C_2, Cr_3C_2 and possibly CrC form as the result of peritectic reactions with the melt. Westgren and Phragmén state that just three carbides form, the one already mentioned (Cr_4C) and Cr_7C_3 and Cr_3C_2. The formula Cr_7C_3 was selected in preference to the Cr_5C_2 of Ruff and Foehr, because it fitted the density and X-ray data much better. There can be little doubt that the only difficulty here is that of allocating the formula to this phase. Westgren and Phragmén also examined the microstructure of their preparations and observed that the alloys containing from 4.5 to 8 per cent. carbon solidify by a peritectic reaction. It is of interest to note that they found HCl to be incapable of showing up the reaction rings or envelopes of one carbide about another, so that for this purpose they used boiling sulfuric acid. The carbon-rich carbide that is satisfactorily identified as Cr_3C_2 has been recorded by Moissan, Ruff and Foehr, and Westgren and Phragmén. In particular, the latter authors point out that this formula agrees with the X-ray and density data.

The carbides of chromium given in Table 2 may or may not be correct. The microscopical and X-ray examinations of Westgren and Phragmén have been given most weight in making this selection but, admittedly, the identification of the first two carbides is contradicted by the work of others. Our knowledge of the phase relationships existing between them is, of course, incomplete, which is not difficult to understand in view of the known sluggishness of peritectic reactions and the interference of oxygen or chromic oxide in this system (Nischk).

[6] A. Westgren and G. Phragmén: Roentgen Analysis of the Chromium-Carbon System. *Kungl. Svenska Vetenskap. Hand.* [3] (1925) **2**, 3.

[7] O. Ruff: On Carbides. *Ztsch. f. Elektrochem.* (1918) **24**, 157.

[8] O. Ruff and T. Foehr: On the Chromium-Carbon System. *Ztsch. f. anorg. Chem.* (1918) **104**, 27.

[9] K. Nischk: Studies of the Reactions between Metals and Oxides and Carbon. *Ztsch. f. Elektrochem.* (1923) **29**, 373.

[10] O. Ruff: Discussion of K. Nischk. *Ztsch. f. Elektrochem.* (1923) **29**, 469.

No carbide of chromium has been reported as having great hardness, except that Friederich and Sittig report a fused alloy containing 3 per cent. C, which scratches corundum.[11]

Since this was written the paper by Kraiczek and Sauerwald[12] on the chromium-carbon system has been received. They report a diagram which is similar to that of Ruff and Foehr, with a eutectic at 1475° C. and 4.5 per cent. C between chromium, with 0.9 per cent. C in solution and a carbide which agrees well with Cr_5C_2 (theoretical C = 8.45 per cent.) There was no evidence of Cr_4C and Cr_2C. The carbide Cr_3C_2 was again found, as well as an intermediate phase which extends from 9.25 to 9.9 per cent. C and which is a solid solution, somewhat as was found by Nischk. This solid solution was found to have a transformation. This work throws considerable doubt on the existence of Cr_4C, but on the other hand, the diagram disagrees with the microscopical data of Nischk and of Westgren and Phragmèn. At present it seems impossible to reconcile all of these inconsistencies.

Carbides of Molybdenum

Molybdenum is known to form the carbide Mo_2C, while a second carbide, MoC, and others have been reported. Moissan heated molybdenum in contact with carbon until the melt was saturated and found that carbon combines with molybdenum in the proportion required by Mo_2C. Any excess carbon was thrown out as graphite. Williams had already reported that WC forms in the presence of iron,[13] so that it is likely that experimenters were on the lookout for a carbide, MoC, and, in fact, Moissan and Hoffmann soon reported that MoC forms in the presence of aluminum, or aluminum carbide.[14] It is a gray powder of prismatic crystals with a density of 8.4 and a hardness of 7 to 8. Their samples ran 11.5 to 12 per cent. C as compared to 11.12 per cent. C theoretical.

The methods that were used in the early work for carburization were not all that could be desired, and Hilpert and Ornstein[15] sought a method that would more certainly produce the higher carbides of molybdenum (and tungsten). To this end they carburized molybdenum powder in a stream of carburizing gas to the limit of absorption. This composition

[11] E. Friederich and L. Sittig: Production and Properties of Some Binary Carbides. *Ztsch. f. anorg. Chem.* (1925) **144**, 169.

[12] R. Kraiczek and F. Sauerwald: The System Chromium-Carbon. *Ztsch. f. anorg. Chem.* (1929) **185**, 193.

[13] P. Williams: Sur la préparation et les propriétés d'un nouveau carbure de tungstène. *Compt. rend.* (1898) **126**, 1722.

[14] H. Moissan and M. K. Hoffmann: On a New Molybdenum Carbide, MoC. *Ber. Deutsch. Chem. Gesell.* (1904) **37**, 3324.

[15] S. Hilpert and M. Ornstein: On a Simple Method of Preparing Molybdenum and Tungsten Carbides. *Ber. Deutsch. Chem. Gesell.* (1913) **156**, 27.

was indicated as MoC although there was some evidence of a higher carbide, Mo_2C_3. The carbide Mo_2C was also found, as was to be expected. No mention was made by them of a proper and sufficient identification of these carbides and later work has not brought a satisfactory conclusion here.

Westgren and Phragmén subjected homogenized alloys of molybdenum and carbon to X-ray analysis in an attempt to identify the phases which form.[16] Besides the molybdenum they found a phase which crystallized with the hexagonal close-packed type of atomic arrangement, containing about 30 atomic per cent. carbon. Contrary to other investigators, they concluded that this phase was a solid solution of carbon and molybdenum instead of being a compound, Mo_2C. It was said to be slightly variable in composition, and this was given as one of the reasons for assuming the phase to be a solid solution, in conjunction with the expansion of the lattice which is produced when the carbon content of this phase is increased. This stretching makes the molybdenum lattice larger than the tungsten lattice in the corresponding phase of the tungsten-carbon system, even though the lattice of pure molybdenum is smaller than that of tungsten. This they have found to be exceptional among intermetallic compounds. Their final argument in favor of the solid-solution theory was that the diffraction pattern was that of an element which crystallized with the hexagonal close-packed arrangement of spherical atoms, a point which was subsequently answered by Becker. The carbon atoms would not occupy positions on the lattice, but would be "forced" to occupy positions between the molybdenum atoms similarly to the carbon atoms in the gamma iron solid solution. Without attempting an extended argument here, their analogy to the gamma iron solid solution which forms on carburizing iron below the transformation point is not convincing. This gamma solid solution is the same phase as pure, or carbon-free, gamma iron, while the carburization of molybdenum produces a new phase which is stable with molybdenum over intermediate concentrations. Their picture of the carburization of iron below the transformation point does not alter this, although, of course, when iron is treated in that way, carburization is accompanied by a phase change (Arnold). Granting that the carbon content of this MoC phase is variable, it seems quite in line to consider this phase as essentially Mo_2C, a compound, with some solubility for molybdenum. Except for the solubility feature, this is the point of view of Becker for the analogous case of W_2C, which will be discussed later.

Friederich and Sittig[17] give two carbides of molybdenum, whose properties are included in Table 2. The Mo_2C is not very hard while the

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[16] A. Westgren and G. Phragmén: Roentgen Analysis of the Systems Tungsten-Carbon and Molybdenum-Carbon. *Ztsch. f. anorg. Chem.* (1926) **156,** 27.

[17] E. Friederich and L. Sittig: *Op. cit.*

chief difference in the preparation of Mo_2C and MoC seems to be that the former was made at 1200° C. and the latter at 1500° to 1600° C. Takei reports that Mo and Mo_2C form a eutectiferous series and that both the Mo and Mo_2C phases are slightly variable in composition.[18] The atomic arrangement of MoC has not been reported and until that phase receives X-ray identification there must linger some doubt as to its composition and constitution.

Tungsten-carbon System

Coming to the tungsten-carbon system we find that two carbides, W_2C and WC, have been reported, and the evidence is such that we can entertain no doubt as to their occurrence. Moissan produced W_2C, but he evidently failed to produce any higher carbide. On saturating the melt with carbon, he found the carbide W_2C and graphite. We now know that the higher carbide, WC, decomposes on melting with the precipitation of graphite and this may account for the failure of Moissan to discover it. WC was first reported by Williams[19] who produced it in the presence of iron and isolated it by physical and chemical means. Hilpert and Ornstein report the first direct production of WC by passing a carburizing gas over tungsten metal powder at an elevated temperature although they believed also that a higher carbide formed, W_3C_4, which contained about 7 per cent. C.[20]

The first systematic study of the tungsten-carbon system was that of Ruff and Wunsch[21] who reported on the phases and microstructure of alloys that solidify from fusion. They report three eutectics, one of which deserves special mention, as follows: $W-W_3C$ eutectic at 1.4 per cent. C, a metastable ternary eutectic at 2.4 per cent. C, and the $WC-W_2C$ eutectic at 3.5 per cent. C. The identification of these phases was largely chemical and disagrees in the phase W_3C with later work. They showed the peritectic decomposition of WC on melting, with the separation of graphite and the formation of a lower carbide on solidification. They also made it clear why it is that the melt takes up only about 4.5 per cent. C, as has since been stated. This work is of interest in clearly establishing the experimental difficulties involved in studying high-temperature equilibria in this system.

Dr. Saul Dushman and Mrs. Mary R. Andrews, of the Research Laboratory at Schenectady, introduced a new method for studying the carbides of tungsten, which could also be used with other metals that

[18] T. Takei: On the Equibrium Diagram of the Molybdenum-Carbon System. *Sci. Rept.* Tohoku Imp. Univ. (1928) **17**, 939.

[19] P. Williams: *Op. cit.*

[20] S. Hilpert and M. Ornstein: *Op. cit.*

[21] O. Ruff and R. Wunsch: On the Tungsten-Carbon System. *Ztsch. f. anorg. Chem.* (1914) **85**, 292.

can be drawn to filament form.[22] They carburized tungsten filaments by heating them in carburizing gases at low pressures, and thus formed a case of tungsten carbide on a core of tungsten. With this method of preparation, it was possible to follow the change in conductivity during the course of carburization, and this led to the identification of the two carbides W_2C and WC. The former came at a sharp minimum at 7 per cent. of the conductance of pure tungsten and the latter at 40 per cent., or, in other words, two sharp breaks came at carbon percentages corresponding to these two compositions. Their results did not suggest the formation of any other carbides under the conditions employed in the experiments. In a later paper Mrs. Andrews published the curve of conductance versus percentage of carbon in the filament and gave more complete details of methods and results.[23]

With the identification of the carbides of tungsten well established, we may turn to the X-ray work which has given the atomic arrangement. In a paper on the structure of some of these metal carbides Becker and Ebert reported that WC is hexagonal, but they did not attempt to define the lattice further.[24] Westgren and Phragmén[25] reported WC along with a second phase with "somewhat more than 30 atomic per cent. carbon." This latter is presumably the same phase that others have identified as W_2C. They give the lattice as hexagonal close-packed and consider the phase to be a solid solution of carbon and tungsten. In this their views are analogous to the ideas on the corresponding phase of the molybdenum-carbon system. In WC the tungsten atoms are arranged on a simple hexagonal lattice, and it is suggested that the carbon atoms occupy the positions at $(\frac{1}{3}; \frac{2}{3}; \frac{1}{2})$, or in the large spaces between the tungsten atoms. The distance between centers of the tungsten and carbon atoms at the closest approach would be 2.19 Å. This checks well with the sum of the two radii of these atoms ($1.37 + 0.77 = 2.14$ Å), using the size of the carbon atom in the diamond lattice.

The conception of W_2C advanced by Westgren and Phragmén would greatly increase our difficulties in understanding chemical combinations of this character. A discussion of this point would involve the same argumentation used in connection with Mo_2C, but this point has been especially considered by Becker and Holbing,[26] who attacked the problem experimentally. They gave chemical evidence which showed that W_2C

[22] M. R. Andrews and S. Dushman: Reaction Between Naphthalene and Tungsten at Low Pressures. *Jnl. Frank. Inst.* (1921) **192**, 545.

[23] M. R. Andrews: Production and Characteristics of the Carbides of Tungsten. *Jnl. Phys. Chem.* (1923) **27**, 270.

[24] K. Becker and F. Ebert: *Op. cit.*

[25] A. Westgren and G. Phragmén: *Op. cit.*

[26] K. Becker and R. Holbing: Some Properties of the Tungsten Carbide, W_2C. *Ztsch. f. angew. Chem.* (1927) **40**, 512.

is a different phase from either W or WC while the diffraction pattern (powder method) was reproduced to show the structural difference of this phase, although no attempt was made to analyze the pattern. The full weight of the structural evidence to be obtained by X-ray analysis was not brought out until later.

In a report on further work on the carbides of tungsten, Skaupy confirmed the formation of the two tungsten carbides W_2C and WC though he dealt mainly with the production and uses of the carbides.[27] He also gave X-ray evidence of the existence of a new phase which is stable only at high temperatures. An interesting observation was made on the structure of an alloy with 3.8 per cent. C which had been fused under an arc in vacuum. Its macrostructure was that of a coarse-grained aggregate, though it showed a fine-grained, duplex, structure under higher magnifications. This structure was considered by Guertler to be due to a eutectoid inversion in the solid state just below the freezing point.

Following the paper by Skaupy, Becker[28] described the "new phase" as an allotropic modification of W_2C which he called βW_2C. The transformation point from beta to alpha was found to be above 2400° C. The atomic arrangement of βW_2C was not given; αW_2C was reported as having the cadmium iodide structure. A more complete discussion of the carbides of tungsten was given in another paper[29] from which the X-ray data are recorded in Table 1. Becker assumes for W_2C that with the carbon atoms at $(0, 0, 0)$, the tungsten atoms would be at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4} + p)$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4} - p)$ where p is a small correction factor and is equal to about 0.02 Å. This would give the hexagonal close-packed arrangement of the metal atoms found. The closest approach of the W and C atoms would be 2.15 Å, which agrees well with the respective atomic radii. With this demonstration that W_2C has a definite lattice, Becker closes

TABLE 1.—*Lattice Data of Tungsten Carbide*

	Lattice Parameter			Density	Closest Approach of Atoms		
	a	c	c/a	d	W-C	W-W	C-C
WC....................	2.94	2.86	0.973	15.52	2.22	2.86	2.86
W_2C....................	2.99	4.72	1.575	17.15	2 15	2.78	2.99
W....................	3.155			19.32		2.73	
C (diamond)...........	3.52			3.57			1.53

a, c and interatomic distances are in Å; d is in grams per cubic centimeters.

[27] F. Skaupy: On the Carbides of Tungsten and Their Uses. *Ztsch. f. Elektrochem.* (1927) **33**, 487. See also: A New Hard Metal. *Umschau* (1929) **33**, 6.

[28] K. Becker: Constitution of the Tungsten Carbides. *Ztsch. f. Elektrochem.* (1928) **34**, 640.

[29] K. Becker: Crystal Structure and Coefficient of Thermal Expansion of Tungsten Carbide. *Ztsch. f. Phys.* (1928) **51**, 481.

his argument that this phase is a compound and not a solid solution. Other important data given by Becker are reproduced in Table 1.

Calculations of the atomic volumes show that the carbon atoms in these carbides assume the atomic volume of the diamond. Becker seems inclined to ascribe the great hardness of tungsten carbide to this circumstance.

By recording the diffraction patterns of the carbides at elevated temperatures the coefficients of expansion in different lattice directions were determined. Curiously enough the expansion coefficient of W_2C in the direction of the c axis was found to be as low as 1.2×10^{-6} per degree C., or less than one-tenth that usually found for the common metals, and much less than for pure tungsten. The coefficient in the direction of the a axis was 11.4×10^{-6}, while the corresponding coefficients of WC were 5.2 and 7.3×10^{-6} respectively. In another recent paper Becker reviewed the work on the W-C system, but was not yet prepared to give the constitution diagram as based on the newer information.[30]

Summing up the literature on the tungsten-carbon system, we may say that the last few years have seen a quickening in the experimental work done, but that we are not yet ready to combine all the experimental data obtained from different methods of attack into a constitution diagram. In an attempt to clear up the constitution of this system and to reconcile X-ray data with other physical and chemical data, W. P. Sykes, of the Cleveland Wire Division of the General Electric Co., is carefully checking this system.

URANIUM CARBIDES

Uranium is the last element in this group and is known to unite with carbon. Moissan reported the carbide U_2C_3 but we have no account of a systematic study of this system. In a report on uranium steels, Polushkin gave U_2C_3 and UC.[31] Moissan states that U_2C_3 is harder than quartz, but softer than corundum. This carbide is quite unstable in the presence of oxygen; it burns violently in the air and decomposes water readily, with the formation of hydrocarbons. In this respect it is similar to thorium carbide.

DIFFICULTIES IN HANDLING HARD METAL CARBIDES

A study of the literature on the hard metal carbides leaves one with the feeling that the experimental difficulties involved in handling these compounds are rather great. They are due to the high fusion points involved, the marked affinity of some of the elements for such gases as oxygen, hydrogen and nitrogen, and to the frequent occurrence of peritectic reactions on solidification of the melts.

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[30] K. Becker: On the System Tungsten-Carbon. *Ztsch. Metallk.* (1928) **20**, 437.

[31] E. P. Polushkin: Alloys of Iron and Uranium. *Carnegie Schol. Mem.*, Iron and Steel Inst. (1920) **10**, 129.

TABLE 2.—*Data on Hard Metal Carbides*

Carbide	Mohs Hardness	Atomic Arrangement	Lattice Parameters			Density		M.P. Deg. C.	Carbon, Per Cent
			a	c	c/a	Cal.	Obs		
TiC..........	9+	FCC	4.60			4.08	4.25	3250±	20.0
ZrC . ..	8 − 9	FCC	4.76			6.51	6.90	3250±	11.7
ThC₂... ...							8.90		
V₅C........		Hex			0.17				4.5
VC	7 − 9+	FCC	4.30			5.25	5.36	2800	19.0
NbC	9+	FCC	4.40			8.20	7.56	3800+	11.4
TaC ..	9+	FCC	4.49			14.00	13.96	3800+	6.2
Cr₄C . .	7a	FCC	10.64c			7.24	6.75		5.45
Cr₇C₃.......		Hex	13.98d	4.52		6.9	6.9	1665	9.0
Cr₃C₂.	8	Ort	2.82e	11.46		6.66	6.6	1890	13.3
Mo₂C	9+	HCP	2.99	4.72	1.58		8.9	2500+	5.88
MoC	7 − 8		(4.88)	(6.54)	(1.34)f		8.40	2840	11.12
W₃Cb									
W₂C	9+	HCP	2.99	4.71	1.57	17.15g	16.9g	3000	3.15
WC	9+	Hex	2.90	2.83	0.97	15.52g	15.5g	2900	6.12
U₂C₃ . .	8+						11.28		7.03

a Fused carbide with 3 per cent C reported as harder than corundum. (See Footnote 11.)
b Reported by Ruff and Foehr but no properties given
c 120 atoms per unit cell.
d 80 atoms per unit cell
e 20 atoms per unit cell; $b = 5.52$.
f Parameters found by T. A. Wilson for phase not as yet identified as MoC.
g K. Becker: Footnote 29

The preparation of the hard metal carbides has been fully described in the literature and in our work we have used the methods described as well as certain modifications which we have developed for tungsten carbide. Two simple methods are those of heating the mixture of the metal, or its oxide, with carbon in an electric furnace, and fusing the mixture in an arc furnace. In the latter case a carbon crucible may be used, which will serve as the source of carbon. The product obtained can then be tested in the massive form or as a powder. One difficulty that may be encountered here, at times, is due to the strong affinity of some of the metals for the gases, hydrogen, nitrogen, etc. This, as is well known, interferes with the hydrogen reduction of the oxide in the preparation of the pure metal for carburization.

HARDNESS MEASUREMENTS

The hard metal carbides are of interest to us largely on account of their hardness, which places them in a class with the topaz and the sapphire. The usual method of evaluating the hardness of such brittle compounds (mostly minerals) is by the Mohs hardness number. These run from 1 for the softest mineral to 10 for the diamond. This scale is rough and arbitrary and is poorly suited to the determination of small differences in hardness among very hard substances, which will be clear

by reference to Fig. 2. This curve gives the absolute hardness of the various Mohs hardness numbers. The difference between sapphire and diamond (9 and 10) is as great as that between sapphire and talc, so that a statement to the effect that a substance is harder than sapphire (or corundum) is no more discriminating than saying that quartz is harder than talc.

In an attempt to improve this situation we have tried to devise means of securing more accurate or reliable information. Before attempting any more refined methods we tried scratching various hard substances with the fused carbide reguli and, in general, our results confirmed those reported in the literature. We also noted that some of the carbides crumbled on the edge when we attempted to scratch a hard, strong material like cemented tungsten carbide. This suggested trying methods that would utilize the powdered carbide.

Previously we had done considerable work on lapping tests, using boron carbide and silicon carbide and other hard metallic powders, and the same methods were tried to test the hardness of the powdered carbides. A

FIG. 2.—ABSOLUTE VALUES OF THE MOHS HARDNESS SCALE.

standard piece of cemented tungsten carbide was lapped on one side with a fixed quantity of powder under constant operating conditions. The rate of wear on the test block was determined at the end of each minute period, and the figures obtained for different carbides were used to compare the "lapping hardness" of those carbides. Some of the carbides showed very little ability to wear away the test block, while a few were found which were about as effective as WC. Incidentally, the carbide W_2C is appreciably less effective than WC. A second means of comparing the carbides comes from the "feel" of the test block on the disk.

A modified scratch test was also used, which employed the powdered carbide rather than the massive reguli. The test block was a piece of highly polished cemented tungsten carbide.[32] A small amount of powder when crushed on to the surface with a second block of cemented tungsten

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[32] I am indebted to Dr. George F. Kunz for suggesting the use of a polished test block.

carbide produces scratches according to the "scratch hardness" of that powder as related, of course, to the hardness of the polished surface. Here again a few carbides were found which produce rather definite scratches in the cemented tungsten carbide test block.

Both of these tests are time-consuming and require great skill and attention to detail, if reproducible results are to be obtained. Even with good technique and verified results these tests are so new that we would not feel justified in drawing any but general conclusions so far. For these reasons there does not seem to be any test which can be used in this field that is capable of yielding reliable quantitative measurements of the hardness of our superhard materials. We may, however, sum up our work in this field tentatively with the statement that the carbides of V, Ti, Zr, Cr, Mo and U are relatively soft, while the carbides of Ta, Nb and W are relatively hard, but not as hard as boron carbide, which is known to be a good lapping compound for tungsten carbide. Naturally this says but little about the usefulness of these materials, for hardness is but one requirement which they must possess.

X-RAY INVESTIGATION

The field of the hard metal carbides has not been worked over in detail, and its literature recounts discrepancies which are confusing. The situation is such that some positive identification of the materials prepared is desirable, or even necessary, if the results are to be properly catalogued. This identification and control we sought in the determination of the X-ray diffraction patterns, and this new tool of metallurgical research has given valuable results in this field. Our results on the carbides of Ti, Zr, V, Nb, Ta and W agree well with those reported in the literature except that the lattice parameter found at the Research Laboratory is apt to be a few per cent. smaller than that reported. We have found both the hexagonal and rhombic carbides of chromium, as well as a suggestion of a cubic carbide. The former would correspond to Cr_7C_3 and Cr_3C_2, respectively. The cubic form would correspond to Cr_4C which was reported by Westgren and Phragmén, but which has not been identified by those who have studied the system metallographically.

It will be recalled that while MoC has been reported, it is Mo_2C whose identity seems to have been well established. In our work we have secured evidence of a second lattice having a hexagonal close-packed type of arrangement of the metal atoms. This may or may not be the monocarbide, but at present that seems to be the best way to identify this phase, and the lattice parameters have been tentatively included in Table 2 as a matter of record.

In Fig. 1 the carbides of the hard metal carbide group are brought together in their periodic arrangement. This figure is intended to show the shift in atomic arrangement of the metal atoms from the metal to the

carbide. In the first group the metals are hexagonal, while in the second group they are body-centered cubic. In both groups the carbides have a simple arrangement; that is, face-centered cubic of the metal atoms. The difference in atomic weight of the carbon atom and the metal atoms of these compounds is so great that the X-ray diffraction pattern shows only the positions of the metal atoms, which is the arrangement reported in the literature. If the positions occupied by the carbon atoms are to be determined, that must be done by some indirect method of calculation. Inasmuch as the ratio of metal to carbon atoms is 1/1 in the carbides of the first two groups, we may make the simple and obvious assumption that the complete atom arrangement is that typified by the NaCl lattice, which is simple cubic with the Na and Cl atoms alternating. This gives a face-centered cubic arrangement to the metal atoms.

In the third group, carbon forms more complex "molecules" which have a marked tendency to form lattices of lower symmetry. In the carbides of chromium, this tendency becomes more marked as the carbon-atom to metal-atom ratio increases in the compound. On the other hand, the work of Osawa and Oya, to which I have not had access, shows that the carbides of vanadium have just the opposite tendency, for there V_5C is hexagonal and V_4C_3 is given as face-centered cubic. The carbide WC stands out as an exception, from one point of view, as it is hexagonal and not face-centered cubic. One might expect that the atomic ratio of 1/1, which suits these two elements admirably, would correspond to the simpler NaCl type of structure.

Calculation of the size of the metal and carbon atoms can be made on the basis of certain simple assumptions. Thus we have seen from the work of Becker on the carbides of tungsten that the tungsten atom has the same size that it occupies when isolated and that the carbon atom has the size of that atom in the diamond. Calculations of the space between the metal atoms in several of the face-centered cubic carbides show that space to be closely that which is required to accommodate the carbon atom (Table 3).

TABLE 3.—*Spacing in FCC Carbides*

Carbide	Atom Diameter		Sum	*a* of Carbide
	Metal	Carbon		
TiC.....	2.92	1.5	4 42	4.60
ZrC..............	3.23	1.5	4.73	4.76
VC..........	2.64	1.5	4.14	4.30
NbC..........	2.96	1.5	4.46	4.40
TaC.........	2 83	1.5	4.33	4.49

Atom diameters and lattice parameter *a* are given in Ångströms.

The lattices of the chromium carbides are exceptional in that the unit cells are far larger than the size of the "molecule." It does not seem likely that this feature of the atomic arrangement bears any important relationship to the hardness or other common physical properties.

<div align="center">CEMENTED TUNGSTEN CARBIDE</div>

The knowledge of the hard metal carbides which has accumulated over the past 40 years has created but little general interest in them. This is true in the face of the extended use of hard materials in industry and the greatly superior hardness of this group of carbides as compared to our common tool steels. The reason is not far to seek, for it is well known that intermetallic compounds in general, and the carbides in particular, are weak and notoriously brittle. If such materials are required to have strength and toughness, these properties must somehow be conferred upon them without too great a sacrifice in hardness. This is now being done for the tungsten carbide, WC, by cementing fine particles of the powdered carbide by means of cobalt, a strong and tough metal, to form what may be called "cemented tungsten carbide." This product will now be discussed to show what has been accomplished with this new art.

It may be well at this place to call attention to the fact that the commonly practiced metallurgical arts are old, some of them being as old as historic man. If Huntsman, over 100 years ago, had been given the ingredients of our modern high-speed steel, he would have been able to produce tools that would give a good account of themselves even today. The art of producing cemented tungsten carbide, on the other hand, is but a few years old, or is in its infancy. As time goes one and as new information becomes available, our ideas will change and alterations in this art may be made. We may find that some of our present ideas are inaccurate or incorrect. These are matters which must be left to the future. Today I propose to discuss some of the features which have seemed of sufficient interest to warrant experimental study.

<div align="center">PREPARATION OF TUNGSTEN CARBIDE AND COBALT</div>

A specially purified tungsten oxide is reduced in hydrogen under well-controlled conditions, to give an average particle size of about 3 to 8μ. This tungsten metal powder is similar to that used for lamp filaments, X-ray tube targets, and other pure tungsten products. It is mixed with the desired amount of carbon, which we may assume is sufficient to produce the carbide WC, and heated in a non-oxidizing atmosphere to allow the tungsten to take up the carbon. The time required will depend on the temperature used and we have found that 3 hr. at 1500° C. are sufficient. Other methods of carburizing tungsten can be used, as described by earlier workers. It may be of interest to point

out that the phase relationships in the tungsten-carbon system are such that the molten alloy does not take up sufficient carbon to give the carbide WC in a pure state and free from other substances. Becker has stated that about 4.5 per cent. C is the maximum amount of carbon that is taken up in this way and this composition corresponds to a mixture of the two carbides, W_2C and WC. While this composition gives valuable properties, this discussion relates to a higher carbon content.

Cobalt metal powder is prepared from a purified cobalt oxide by reduction in hydrogen. This operation is carried out at a low temperature to retain the powder in a fine state. The reason for this will be apparent from the discussion which follows.

Having produced the two powders separately, they are next mixed in a ball milling operation. In some experiments on the use of porcelain mills with pebbles, porcelain mills with steel balls, and steel mills with steel balls, it was observed that a better product was made when the steel balls were used. It was also observed that the milled powder would not all go through a bolting cloth even though the two starting powders were both much finer than the mesh of the cloth. A test with a magnet showed that the metal remaining on the cloth was magnetic, while a chemical test gave a strong reaction for cobalt rather than for iron which might have come from the mill. The conclusion seemed obvious that the hammering action of the steel balls had united individual particles of cobalt, and if that were so it also seemed likely that cobalt was being smeared on the particles of tungsten carbide either collectively or individ-ually to form a cobalt envelope. It was then predicted that it would be possible to pick up all of the milled powder with a magnet, even though only the cobalt is magnetic. The verification of this prediction strengthened the envelope hypothesis.

If both agglomeration and smearing occur during milling, we may assume that milling should be continued until the carbide particles are properly coated, although it may be necessary to carry it further to get optimum results. This additional milling may crush up the coarser carbide particles and coat them, and it may also agglomerate the smaller particles into larger masses. From this it is apparent that the particle size of the powder and the distribution of the particle sizes must exert an important influence on the milling time required to give the best results, and hence upon the properties of the cemented material. In practice, this factor is controlled by selecting the powder, or the treatment for producing the powder, and the proper schedule of operations which gives the best results.

The operation of pressing the milled powder may be rapidly passed over, but it may be of interest to note that the cobalt smear or envelope serves effectively to produce quite satisfactory pressing properties in a metal otherwise difficult to handle.

If the pressed bars are fired for $1\frac{1}{2}$ hr. at 800° C. they are made considerably harder and stronger. This temperature is high enough to sinter pure cobalt at least partly, in this time, and we may assume that the hardening is a cobalt effect.[33] Presumably the cobalt envelopes commence to adhere to each other during this low-temperature firing; 50° higher produces a noticeable increase in this effect, which continues as the temperature is raised still further.

The final step in the manufacture of cemented tungsten carbide is that of sintering the pressed bar at a high temperature. A satisfactory theory of this operation must await the establishment of the W-C-Co ternary diagram, or possibly the pseudobinary WC-Co diagram, if such a system actually exists. In the meantime we may set up a hypothesis which gives a working picture of what occurs during sintering.

We now know that the sintering action results in a composite of tungsten carbide particles in a matrix of a cobalt-rich phase, the latter cementing the carbide particles together. This will be made clear by photomicrographs. We have at once two alternatives to account for the mechanism of this cementing operation, both of which are amenable to experimental verification. Either the final sintering is simply an extension of the low-temperature or "cobalt" effect, or else a new, and liquid, phase forms which produces a molten sintering medium.[34]

One might assume that our knowledge of the behavior of cobalt in coating the carbide particles during milling and the behavior of pure cobalt in sintering fully at around 1400° C. would be sufficient to warrant the assumption that the sintering of the cemented tungsten carbide is due simply to the sintering or compacting of the cobalt matrix. Furthermore this material can be fully sintered well below the melting point of cobalt. As a matter of fact, we know that a considerable increase in hardness and density can be produced simply by the "cobalt effect."

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[33] See, for example:

R. C. Smith: Sintering, Its Nature and Causes. *Jnl. Chem. Soc.* (1923) **123**, 2088.

F. Sauerwald: Grain Growth in Compressed Metal Powders. *Ztsch. f. anorg. Chem.* (1922) **122**, 277.

C. J. Smithells, W. R. Pitkin and J. W. Avery: Grain Growth in Compressed Metal Powder. *Jnl. Inst. Met.* (1927) **38**, 85.

T. W. Hagen: On the Welding of Solid Powders by Pressure. *Ztsch. f. Elektrochem.* (1919) **25**, 375.

J. A. Hedvall: On the Physical and Chemical Processes in the Agglomeration of Unmelted Powders *Ztsch. f. phys. Chem.* (1926) **123**, 33.

B. Garre: On the Strength of Pressed Metal Powders on Annealing. *Ztsch. f. anorg. Chem.* (1927) **161**, 152.

[34] F. C. Kelley, of the Research Laboratory, has made a detailed study of this sintering operation, and has rendered great assistance in helping to establish this hypothesis.

On the other hand the reaction, or sintering effect, soon comes to a halt at any one temperature and we should not expect to produce the full hardness at temperatures below 1300° C. This suggests that we are really dealing with a threshold temperature above which it is necessary to heat. This is a good expression of the situation, and we may now consider some of the evidence which supports this view.

First of all we find that cemented tungsten carbide with 13 per cent. of cobalt must be heated above a temperature which can be located at about 1350° C. to produce proper hardness and strength. ·If this temperature is associated with the formation of a liquid phase and its subsequent solidification, the methods of thermal analysis should reveal a heat effect at that temperature. We have found such a point at 1355° C.
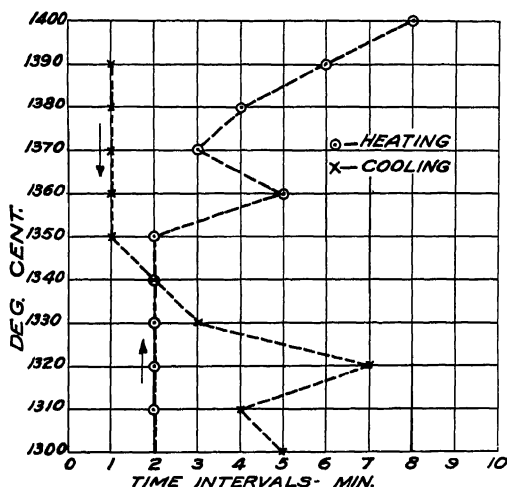
FIG. 3.—THERMAL CURVES.

and this corresponds to the temperature above which it is necessary to heat to produce the complete cementing action. Two representative curves obtained with an optical pyrometer are given in Fig. 3. This close agreement with sintering practice supports the hypothesis here presented.

Such a liquid phase would presumably be a eutectic in the WC-Co system. In a later section of this lecture it will be shown that cemented tungsten carbide does not show a structure that is commonly associated with eutectic solidification and reasons for that will be advanced. However, if we were to treat a mixture of WC and Co powders in eutectic concentrations about as we sinter our standard material, the mass should fuse and the microscope should reveal the eutectic structure. Fig. 4 shows a mixture of 27.5 per cent. WC and 72.5 per cent. Co which has been heated above 1360° C., and the eutectic structure will be recognized at once.

This temperature is well between the melting point of pure cobalt at about 1480° C. and the melting point of the Co–C eutectic which lies at about 1250° to 1275° C.[35] The circumstance that carburization of the cobalt during sintering is conceivable makes it necessary to consider the formation of a cobalt-carbon alloy. Furthermore, the W–Co eutectic melts in the neighborhood of 1450° C.[36] These three possibilities can be eliminated and it seems more likely that Co and WC form a molten eutectic alloy. Carrying out this idea, we may expect that this molten alloy
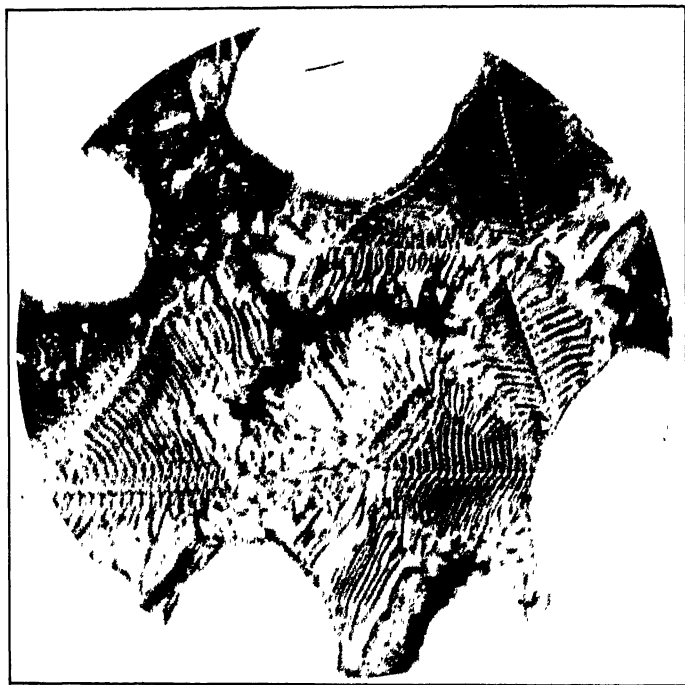
FIG. 4.—EUTECTIC STRUCTURE IN 72.5 Co/27.5 WC HEATED TO 1375° C.   × 1500

wets the particles of tungsten carbide and, by the action of surface tension, sinters the mass together. On the solidification of this eutectic, the WC phase which separates out would be absorbed by the adjacent and larger particles of WC, so that in reality it would be the cobalt-rich phase of the (solid) eutectic that becomes the cement. We may now consider some evidence relevant to this question, which is not incompatible with this viewpoint.

[35] O. Ruff: On the Constitution Diagrams of Carbon with Iron, Nickel, Cobalt and Manganese. *Ber. Deutsch. Chem. Gesell.* (1912) **45**, 3139.

G. Boecker: Investigations of the Cobalt-Carbon System. *Metallurgie* (1912) **9**, 296.

[36] W. P. Sykes: Private Communication.

If cobalt and tungsten carbide unite to form a molten alloy, the finer grains of carbide would be the first to be consumed. Although I would not press the point, I have observed that the microstructure shows fewer small particles than would be expected from the known grain size of the powder, and that of two samples from the same mixed powders, the one showing the greater amount of cement shows fewer of the small particles of carbide. Furthermore, we have frequently observed that cemented tungsten carbide shows more cement under the microscope than should be present were the cement pure cobalt. This observation, of course, would be a demonstration not of liquid solubility of tungsten carbide in cobalt but of solid solubility. But such solid solubility would most likely be produced through the medium of the liquid phase. A study of this point would resolve itself about the purity of the cobalt cement and might be attacked by studying certain physical properties of the cemented material which would reflect the condition of the cobalt, and by thermal analysis. Two physical properties which readily suggest themselves are the magnetic properties and the electromotive force.

The fact that cemented tungsten carbide with 13 per cent. cobalt is magnetic, while the same material after being fused is not magnetic, shows that the cobalt must be in a nearly pure state in the former. Quantitative measurements of the magnetic induction of cemented tungsten carbide, which will be reproduced in a later section, verify the rough test with the permanent magnet. Unfortunately these tests could not be carried up to the point of magnetic saturation, so that we are not privileged to interpret the results in terms of the purity of the cobalt. It is entirely possible that future work will give positive evidence here. Perhaps a better idea is to be obtained from a measurement of the electromotive force. The figures in Table 4 were obtained in an electrolyte of cobalt sulfate dissolved in water, with a tungsten rod as the anode and the sample as the cathode. All measurements were made at the same time, so that the results are comparable among themselves.

TABLE 4.—*Measurements of Electromotive Force.* *Sample/$CoSO_4$/W*

SAMPLE	E.M.F., VOLTS
Pure WC	0.02
Cobalt..	0.17
Fused WC-Co alloy.	0 05
Cemented tungsten carbide..	0.14 to 0.20
Poor grade of cemented tungsten carbide.	0.11

Check measurements were made on a number of random samples of cemented tungsten carbide, which are designated in Table 5 as 1, 2, etc. Pure cobalt and pure WC are also included. The voltage was measured with a potentiometer and was followed with time. Two values are given in each case, one for zero time and one representing the constant value.

A platinum electrode was used and the electrolyte was 0.1 M solution of $CoCl_2$ in water.   These results are recorded in Table 5.

TABLE 5.—*Measurements of Electromotive Force.   Sample/$CoCl_2$/Pt*

Sample	E.M.F. Zero Time, Volts	E.M.F. Constant Value, Volts
Cobalt.....	0 59	0.64
1.....	0 56	0.60
2	0 51	0.60
3....	0.50	0.58
4	0 45	0.54
5.	0.43	0.53
WC	0 25	0.08

The fused alloy is not greatly different from fused tungsten carbide, while cemented tungsten carbide gives about the same electromotive force as pure cobalt, though it is lower.   This latter fact is consistent with the assumption that the cobalt retains some WC in solid solution.

At a later date it may be profitable to return to a more precise theory of the cementing action, after we understand the requirements of the phase relationships and the constitution of this system, but we may now consider some of the observed effects in the light of the hypothesis as set up.

If a complete cementing action depends on the formation of a liquid cobalt-tungsten carbide alloy, we may expect to find that a low cobalt content will require a higher sintering temperature to produce the best cementing effect.   The amount of liquid eutectic formed at 1355° C. or thereabouts would not be sufficient to permeate the mass of carbide grains, and it would be necessary to produce more liquid phase by going to higher temperatures.   This has been found to be the case, but not without some misgivings that the higher sintering temperature would defeat its own purpose by spoiling the product.   It was early found that sintering the higher cobalt mixtures at temperatures above 1400° C. produces blisters in the metal and that this effect was exaggerated by the presence of free graphite in the carbide used.   The cobalt content of the mixture was 13 per cent.   Presumably the cobalt took up the excess carbon at the high temperatures, and also from the furnace atmosphere, and produced an excessive amount of liquid phase.   The blisters would represent "sweating" in the initial stage, while anything that would lower the amount of liquid would lower the tendency to blister.   We found subsequently that if the cobalt content were lowered, sintering could be carried to higher temperatures without producing blisters and even in spite of the presence of free graphite.

By the same token an increase in the amount of cobalt should produce the opposite effect and increase the tendency to blister and sweat.   A

mixture with 30 per cent. Co, for example, forms so much liquid when sintered in the usual way that it sweats profusely, while mixtures with still higher percentages lose their shape completely.

This sintering hypothesis centers about the formation of a liquid phase, which is presumably a eutectic of Co and WC. Even though this view seems now to be the most reasonable one to adopt, we should not overlook the "cobalt effect" with which we could account for the major portion of the effect observed. If sintering could be carried out at higher temperatures, say at 1400° C. or above, without producing a liquid phase, we might accomplish the full sintering effect, and this would not be inconsistent with the observations made on material that has been sintered at lower temperatures.

STRUCTURE OF CEMENTED TUNGSTEN CARBIDE

Our ideas on the nature and behavior of cemented tungsten carbide have, in many cases, come from a study of its structure, both macrostructure and microstructure. The results obtained have confirmed or strengthened conclusions which have been suggested by other considerations, and in all cases a study of the structure has afforded a powerful tool in the pursuit of these investigations.

The preparation of microsections of cemented tungsten carbide has presented some new and unique problems, not the least of which are those arising from the extraordinary hardness of the material. Extreme fineness of grain and lack of ductility have added to these difficulties.

The first publication dealing with the structure of these materials is that of Schroeter,[37] whose name is indelibly associated with this product, in which he discusses the use of silicon carbide and the older methods of diamond lapping for polishing these materials. The tools and equipment of the lapidary shop are not readily available and we find Gregg and Küttner[38] using various grades of alumina and the commonly practiced methods of preparing microsections, in spite of the immoderate consumption of time involved. While Gregg and Küttner did not comment on the use of silicon carbide for polishing microsections, it has been my experience that this polishing compound always leaves the surface in a pitted condition. At first we had no indication that this was a polishing effect and we were inclined to ascribe it to the characteristics of the metal itself.

A method of preparing microsections of cemented tungsten carbide which has given entire satisfaction was described in an earlier paper.[39]

[37] K. Schroeter: Technology of the Metallographic Examination of Very Hard Alloys. *Ztsch. f. Metallk.* (1928) **20**, 31.

[38] J. L. Gregg and C. W. Küttner: A Metallographic Study of Tungsten-carbide Alloys. *Trans.* A. I. M. E., Inst. Met. Div. (1929) 581.

[39] S. L. Hoyt: Preparation of Microsections of Tungsten Carbide. *Trans.* Amer. Soc. Steel Treat. (1930) **17**, 54.

This method is based on the preliminary preparation of the surface with boron carbide powder and a final polish with diamond dust and employs common polishing technique. The dust used for the final finish is prepared by the General Electric Co. It has a particle size of about 0.5 μ, or 0.00002 in. Coarse particles which might destroy the finish are eliminated by a centrifuging operation. The use of this method soon revealed the true nature of cemented tungsten carbide and showed, among other things, that a plane mirror finish could be prepared which was satisfactorily free from scratches, pits and other polishing defects.

For excellence of results and speed of polishing, a properly graded and fine-grained diamond dust has no competitor in this field, while lapping with boron carbide accomplishes the preliminary operation with equal satisfaction. Diamond dust would seem to be too expensive for use as a polishing powder, but it is not, as we have found that one carat of dust is sufficient to polish 1000 sq. cm. of surface.

Purely superficial effects may falsely give an appearance similar to a true metallic structure. These effects may come from the unsuspected presence of grease or oil while it is quite within the realm of possibility for the surface to become charged with the fine diamond dust. Due to the circumstance that the true structure of this material cannot be known in advance (in fact, it was a mystery for a long time) the effects observed require most careful study to eliminate the false. These precautionary statements are thrown out not so much for the careful student with time and means at his disposal to make a thorough analysis of this problem as for those whose time is limited to a hasty examination of cemented products.

The methods of etching used are in general those which have been developed for tungsten products. Possibly the simplest method of developing the structure is by etching in boiling hydrogen peroxide, but this reagent does not bring out the cement properly and the appearance of the etched surface suggests that some of the fine grains have been dissolved out. These difficulties may be overcome by using potassium ferricyanide that has been made basic by the addition of sodium hydroxide. This reagent is very satisfactory if the cementing action is complete, or if each grain of tungsten carbide is completely surrounded by cement. The 10 per cent. solution requires 5 to 15 min. at room temperature and about 5 to 10 sec. at 80° to 90° C. This reagent does not bring out the tungsten carbide grains by direct attack and if the carbide occurs in clusters, or some of the particles are composed of two or more grains, the structure of the carbide constituent can be developed by an electrolytic etch in a weak electrolyte of 0.5 per cent. sodium hydroxide in water with a low current density. Not more than one second is required to bring out the structure, while longer etching soon develops pits by attacking the cement. Those who are accustomed to the use of the electrolitic etch

will undoubtedly prefer it to the potassium ferricyanide etch, but for an examination of the standard cemented tungsten carbides, others will find the latter a simpler reagent to master.

A mixture of hydrofluoric acid and nitric acid has been recommended for etching materials of this type. We have used a solution of three parts of 30 per cent. hydrofluoric acid in one part of concentrated nitric acid for etching samples containing less carbon than that represented by the carbide WC, or between 3 and 6 per cent.

Two features of the gross structure of cemented tungsten carbide require special mention. The first of these is the surface structure, which may be altered by the action of the furnace atmosphere on the heated material.

The cobalt and tungsten carbide powders are uniformly mixed and are carefully handled in the pressing and sintering operations, so that, in practice, the finished material has a fine-grained, homogeneous structure, with little surface skin, all of which is to be desired. However, taking a broad viewpoint, it must be recognized that a material whose chemical composition is such that it can be altered by both oxidation and decarburization and which is heated in the course of its production and use, is apt to be affected by such treatment. It is the aim during such operations and the object of certain precautionary measures to keep such effects at a harmless minimum. In the laboratory we study such effects by the expedient of greatly exaggerating them, and some of the experience thus gained will be discussed on account of the light thrown on this field of metallurgy.

If a transverse fracture or a polished microsection is dipped in a water solution of copper sulfate, copper deposits uniformly over the section. This reflects the uniform distribution of the cobalt, which deposits copper out of the electrolyte by substitution. Some samples deposit copper preferentially around the outer edge of the section, forming a copper frame. This selective action is presumably due to a segregation of cobalt at the surface. Also, such samples on which a thick "skin" has been deliberately produced may show a very coarse-grained structure. While the initial cobalt content of the sample was 13 per cent., the cobalt of this coarse-grained outer layer may run as high as 30 per cent. and over.

As an example of this effect we may take the following. A 20-gram test sample of cemented tungsten carbide containing 13 per cent. cobalt was heated for 20 hr. at 1375° C. in hydrogen. The sample was on an alundum boat and was exposed to the action of the gas passing over it. At the end of this time the skin which had formed amounted to about 25 per cent. of the whole, while the loss in weight on sintering was slightly over 1 per cent. This loss might be due to oxidation produced by water vapor in the hydrogen and volatilization of the oxides formed, or to decarburization from both hydrogen and water vapor, or to both. Analyses

of the various materials were made in an attempt to determine the mechanism of the action, with the results shown in Table 6.

TABLE 6.—*Analyses of Materials*

	Tungsten, Per Cent.	Carbon, Per Cent.	Cobalt, Per Cent	Total, Per Cent.
Original material (type composition)	82.3	5.2	12.5	100.0
Skin................................ ...	75.84	0.96	18.0	94.8
Interior	84 4	5.63	9.2	99.2

The features of these analyses are the decarburization of the surface, the concentration of cobalt at the surface, the impoverishment of cobalt at the center and the failure of the tungsten, carbon and cobalt to add up to 100 per cent. Obviously the surface has been decarburized, while if we make the reasonable assumption that the missing 5.2 per cent. is oxygen that has been taken up from the furnace atmosphere, and is now present as tungsten oxide, we may ascribe the loss in weight largely to loss in tungsten, which has been oxidized and evaporated from the surface. Inasmuch as the measured loss is the total loss from the whole sample, while the actual loss came solely from the skin, we might look to this loss in tungsten as being responsible for the concentration of the cobalt at the surface. A simple calculation shows that if this were the sole factor responsible for the cobalt concentration, the skin could not be greater than about 5 per cent. of the total sample, instead of 25 per cent. The drop in cobalt at the interior also negatives such an assumption.

I believe the clue to the solution is to be found in the coarsely crystalline and metallic condition of the skin and on the basis of the effect described by Mr. Kelley last year[40] on the coarse crystallization which accompanies metallic diffusion under certain conditions, we may set up the following picture. The furnace atmosphere undoubtedly decarburizes the tungsten carbide particles at the surface and converts them in whole, or in part, into tungsten. At the temperature involved these tungsten particles are able to absorb cobalt from the liquid matrix and form a tungsten-cobalt alloy. Due to the conditions of the formation of this alloy a coarse-grained and columnar crystallization is formed. This outer layer acts as a sump for the cobalt and extracts cobalt from the interior, as is shown by the analysis. Just as steel is exposed to conditions of oxidation, decarburization, "burning," etc., from which it must be protected, we see that cemented tungsten carbide must also be protected from conditions that may injure it.

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[40] F. C. Kelley: Grain Growth in Metals Caused by Diffusion. *Trans.* A. I. M. E., Inst. Met. Div. (1928) 390.

As the second feature of the gross structure we have the cavities which have been previously mentioned by Schroeter.[41] They form during the sintering operation, during the shrinkage, and are probably due to gas or to impurities. It is easy enough to picture the action of gas in this connection but this may not hold for impurities. The formation of a liquid phase, which wets the surface of the carbide particles, sets up tensile forces of surface tension that tend to pull these particles together. The magnitude of the sintering force is at all places equal to the surface tension. If there were nothing to interfere with those forces—i. e., if they were equal at all points, or in all directions—the packing of the particles would be complete except for the circumstance that there is probably but little tendency for the particles to rotate, and thus to improve the packing. If the packing were perfect no voids would occur. From this we may infer that something locally has interfered with the surface tension, or with the wetting of the particles. Small amounts of impurities may be looked to as the most likely sources of this effect. A surface film of very small magnitude or tenacious oxide film, or even a massive impurity, might prevent the wetting of the liquid cement and thus introduce a locality of low cohesion between liquid and solid. An example of the latter effect may be seen in Figs. 6 and 10. Near the center of Fig. 10 there is a cavity which contains a massive impurity. Allowing for the difference in magnification, it is evident that this cavity is as large as many of those shown in Fig. 6.

A study of a reasonably large number of samples of all kinds and from many different sources has shown that the number, size and distribution of these voids varies considerably with the material and with the specific conditions under which the material was prepared. Sometimes they may be present in sufficient quantities to lower the density; at others, few voids are to be seen. The conditions responsible for void formation and the precautions that must be observed to keep them at a satisfactory minimum must be understood by the producers of these products, but a discussion of this phase of the problem lies outside the scope of this lecture.

A more minute study of these voids can be made by reference to Figs. 5 and 6 and to Figs. 15 and 16.

Coming to the fine structure, we may consider the particle size of the carbide constituent. Tungsten carbide powder is made from tungsten metal powder. The carburizing process and the temperature involved suggest that the average particle size is likely to increase, mainly at the expense of the smaller particles. It is, indeed, a matter of common observation that the carbide powder comes from the carburizing treatment in a loosely coherent condition. This suggests that some amount of agglomeration has occurred, even though the temperature employed

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[41] K. Schroeter: *Op. cit.*

is far below the sintering temperature of tungsten carbide. It would not be safe to infer that this sintering effect is necessarily accompanied by particle growth, which would alter the particle size of the powder,
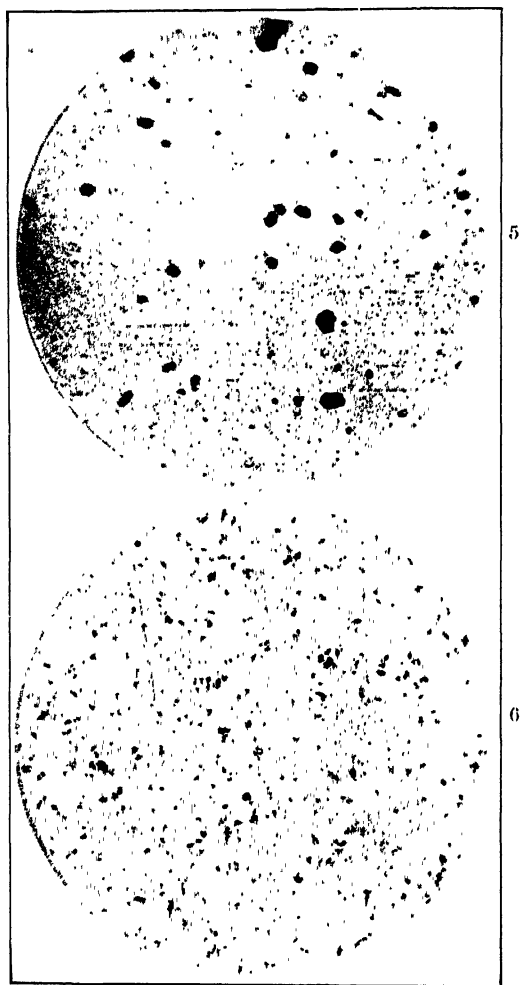
FIG. 5.—DIAMOND-POLISHED SURFACE SHOWING VOIDS.   × 65.
FIG. 6.—SAME AS FIG. 5.

for Sauerwald and Jaenicken have shown that the maximum of this strengthening effect is reached on raising the sintering temperature before recrystallization begins.[42] However, determinations of the

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[42] F. Sauerwald and E. Jaenicken: Strength and Density of Compressed Metal Powders.—III.   *Ztsch. f. Elektrochem.* (1924) **30**, 175.

F. Sauerwald and E. Jaenicken: Power of Adhesion Between Metallic Surfaces. *Ztsch. f. Elektrochem.* (1925) **31**, 18.

particle size of the tungsten powder and of tungsten carbide after carburization do suggest that some grain growth does occur.

The effect of the ball milling operation on the particle size is left somewhat in doubt, on account of the agglomerating effect of the cobalt, which makes it difficult to determine the particle size after milling. The particle size of the finished product can, of course, be determined by a microscopical method, but the relation to the particle size of the tungsten carbide powder is distorted by the ball milling operation. It is perhaps a fair statement that both small and large particles of the original tungsten carbide are missing in the finished product. The larger sizes probably disappear during the ball milling, while the smaller sizes are most likely the particles of carbide that become incorporated in the cement. It might be objected here that the microscope shows some large grains of tungsten carbide in the finished product, but those have undoubtedly formed during sintering. We shall see at once that the mechanism of absorption of tungsten carbide from the molten matrix when it solidifies offers a ready means for accounting for grain growth during sintering.

The cement constituent is one of the principal structural features of cemented tungsten carbide. The milling operation produces intimate contact between the cobalt and the carbide, and this is further enhanced by the pressing operation. On the assumption that cobalt and tungsten carbide form a eutectic at about 1350° C., we may picture the cobalt uniting with the adjacent, fine-grained carbide particles to form a molten eutectic alloy. The fineness of the constituents and their intimate contact make this behavior seem as possible here as in ordinary eutectic fusion, on account of the structural analogies which exist between the two bodies. On the further assumption that this molten alloy wets the carbide particles, we may also picture the molten alloy filling the interstices and completely surrounding the carbide particles. The molten cement may attack the remaining carbide particles to some extent and so affect their size and shape, but it seems more likely that the cobalt becomes saturated with tungsten and carbon under the existing conditions and that this liquid is relatively inert to the remaining particles.

As the net result of this action we may expect to find fewer of the small particles of the carbide left, with the cement filling in the space between those remaining. This is confirmed by the microstructure of cemented tungsten carbide.

Mention of the formation of a eutectic alloy suggests that a eutectic structure might be expected in the cement. It has been our observation that such a structure is never found in standard cemented tungsten carbide. In seeking an explanation of this fact, I was reminded of some structures I had observed in copper-tin-zinc alloys, which may be seen in the *Journal* of the Institute of Metals for 1913, No. 2. A reproduction of these photographs on a larger scale appeared in the *International*

Zeitschrift fur Metallographie for 1914.   Fig. 22 of the latter paper shows a eutectoid structure of alpha and gamma in the presence of alpha.   The white bands of gamma surrounding the primary alpha contain no alpha, an effect which we may ascribe to the fact that the eutectoid structure formed later than the primary structure.   The larger alpha grains have absorbed the alpha constituent of the eutectoid as it formed. Areas of gamma as broad as 6μ are observed which contain no alpha, while if two primary alpha grains come as close together as 3μ no eutectoid structure forms between them.   Returning to the cement structure in our present material, measurements show that areas of cement seldom run up to 2μ across.   While this figure is not to be directly compared to that cited above, it seems reasonable to assume that the presence of free carbide would effectually inhibit the formation of the typical eutectic structure under these circumstances.

It is evident that a certain minimum amount of cementing material is required for sintering and to cement the tungsten carbide grains together, while it is equally evident, on the basis of the hypothesis presented, that this amount of cement can be produced either by adding a correspondingly large amount of cobalt and sintering just above the eutectic temperature, or by adding a smaller amount of cobalt and sintering at an appreciably higher temperature.   In the latter case the cobalt added will dissolve tungsten carbide in excess of the eutectic composition, and in amounts that will depend on the temperature selected and the time of holding at temperature.   On cooling, this carbide would precipitate out on adjacent carbide particles.   Under the microscope we would expect to see thinner cement films and but small differences in structure unless we were able to differentiate between cements of different compositions.

It has been my observation that cobalt contents of over 20 per cent. produce masses of free cement which, incidentally, coincides very closely with the limiting composition at which cemented tungsten carbide loses its remarkable cutting efficiency.

While this discussion does not present all of the interesting points involved, it is sufficient to account for many of the properties and characteristics of this material.   We may now pass to a more general discussion of the structure of cemented tungsten carbide and see, by means of some selected photomicrographs, the appearance of the structures that have been described.

Most metallographers are accustomed to examining metals and alloys which have solidified from the molten state and which may have been altered structurally by some subsequent operation such as heat treatment or mechanical working.   The structures are well known and have been classified into definite systems which form a substantial field of metallography.   From the structures observed, the history of the metal and

other important features are to be read by the skilled observer. In our present case the guide furnished by the historical development of metallic microscopy is lacking because these materials do not pass through the usual cycles of fusion, solidification and transformation.

The fine structure of cemented tungsten carbide is shown in Figs. 7 to 16, which will illustrate the points mentioned. These samples were all prepared by the methods discussed above and were etched with potassium ferricyanide or electrolytically in dilute sodium hydroxide. The tungsten carbide is colored slightly in contrast to the cement. When the high magnification is recalled, the extremely fine grain of this material is obvious.
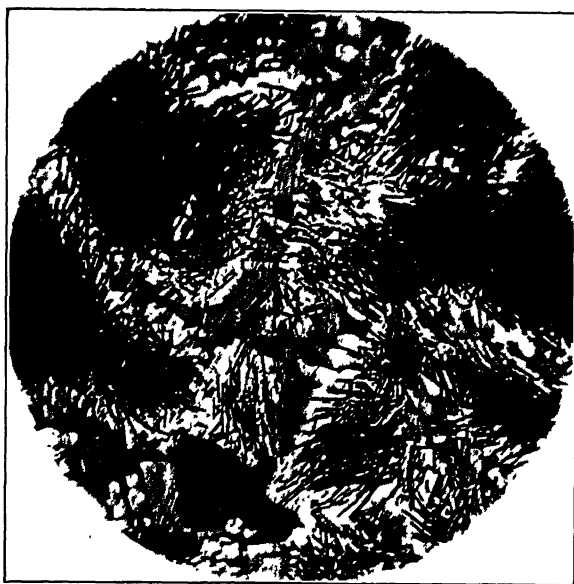
FIG. 7.—CAST CARBIDE.   × 1000.

The carbide particles are oriented at random and suggest the effect we used to see in kaleidoscopic figures. By and large we might assume that many of these grains have carried through from the milling operation. Many others, however, must have been materially altered in both size and shape by the sintering operation, as in Fig. 12. The tendency of the cement is to form a continuous network which completely surrounds the carbide grains and an inspection of the structures shows that this tendency is realized to a satisfactory degree.

Two photographs have been added (Figs. 15 and 16) to show the appearance of a cavity in the etched microsection, at a low-power and at a high-power magnification.

PROPERTIES OF CEMENTED TUNGSTEN CARBIDE

Transverse Strength

Many substances are known which are harder than even our hardest tool steel, sometimes several fold. As examples of these hard materials that find a use in industry, we have industrial diamonds and sapphires,

FIG. 8.—CEMENTED TUNGSTEN CARBIDE, $K_3Fe(CN)_6$ ETCH.   × 1200.
FIG. 9.—CEMENTED TUNGSTEN CARBIDE, ELECTROLYTIC ETCH.   × 1200.

silicon carbide, aluminum oxide, and others. Only to a limited extent do these substances replace or compete with tool steel and the reason for this is that they are not or have not been made strong enough to withstand the stresses which are so commonly imposed on tools. Cemented tungsten carbide, while belonging to the class of superhard materials, possesses remarkable strength, and we may say that the particular feature which gives it its present interest is the fact that it has been

made strong enough for many industrial purposes without sacrificing too much of its hardness.   Therefore it is of interest to determine the strength of this material.

Possessing no ductility, cemented tungsten carbide is tested by breaking a transverse test bar and calculating the modulus of rupture, or maximum stress in the outermost fiber.   The strength thus measured has already been reported[43] as being over half that of high-speed or tool steel, or of the order of 225,000 to 275,000 lb. per sq. in.   These figures have even been exceeded in certain instances.   The same figure is about 425,000 for high-speed steel, according to d'Arcambal[44] while carbon tool steel, tested at the Research Laboratory, ran just over 500,000 lb. per square inch.
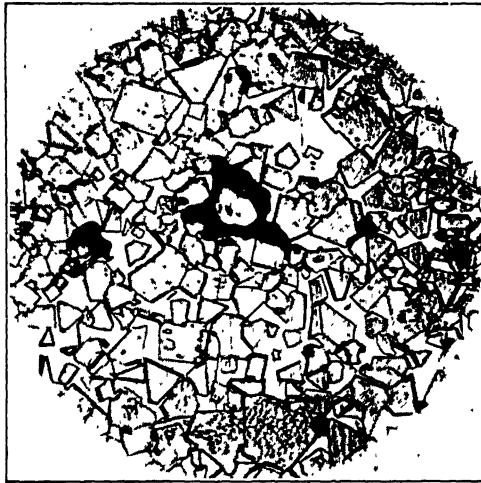
FIG. 10.—CEMENTED TUNGSTEN CARBIDE.   × 1200.

This value depends to some extent on the cobalt content of the material, and this relationship is shown in Table 7.

The treatment which individual compositions receive also affects the strength.   This applies particularly to the sintering treatments and to special heat treatments, after the regular sintering treatment.   Rapid quenching from temperatures in the neighborhood of 1000° C., for example, has been found to lower the strength to well below 100,000 lb. per sq. in.   Quenching from the normal sintering temperature has been found to be without harmful effect.

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[43] S. L. Hoyt: Tungsten-Carbide, a New Tool Material.   *Trans.* Amer. Soc. Steel Treat. (1928) **14**, 695.

[44] A. H. d'Arcambal: Physical Tests on High Speed Steels.   *Trans.* Amer. Soc. Steel Treat. (1922) **2**, 586.
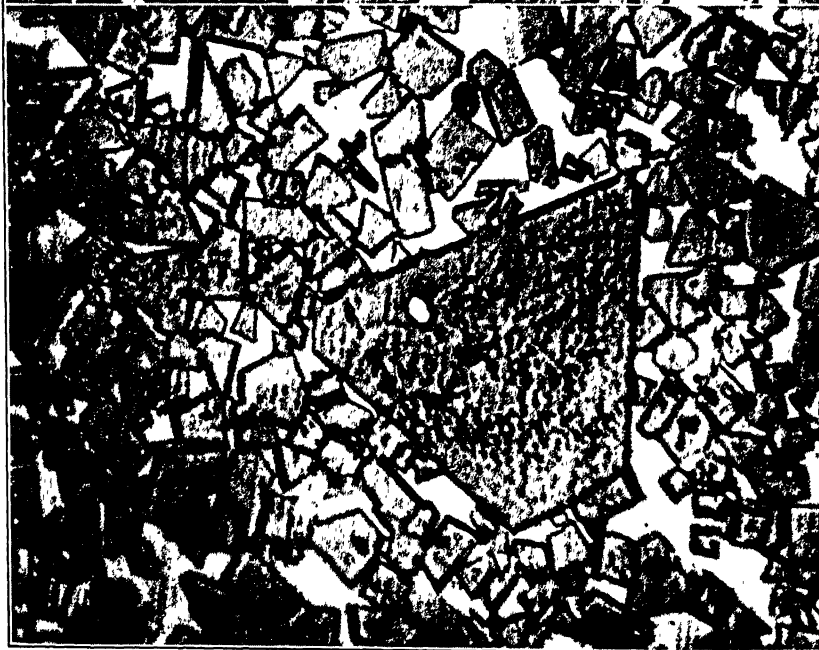
FIG. 11.—CEMENTED TUNGSTEN CARBIDE, 13 PER CENT. Co.   × 2500.
FIG. 12.—CEMENTED TUNGSTEN CARBIDE, 13 PER CENT. Co.   × 2500.
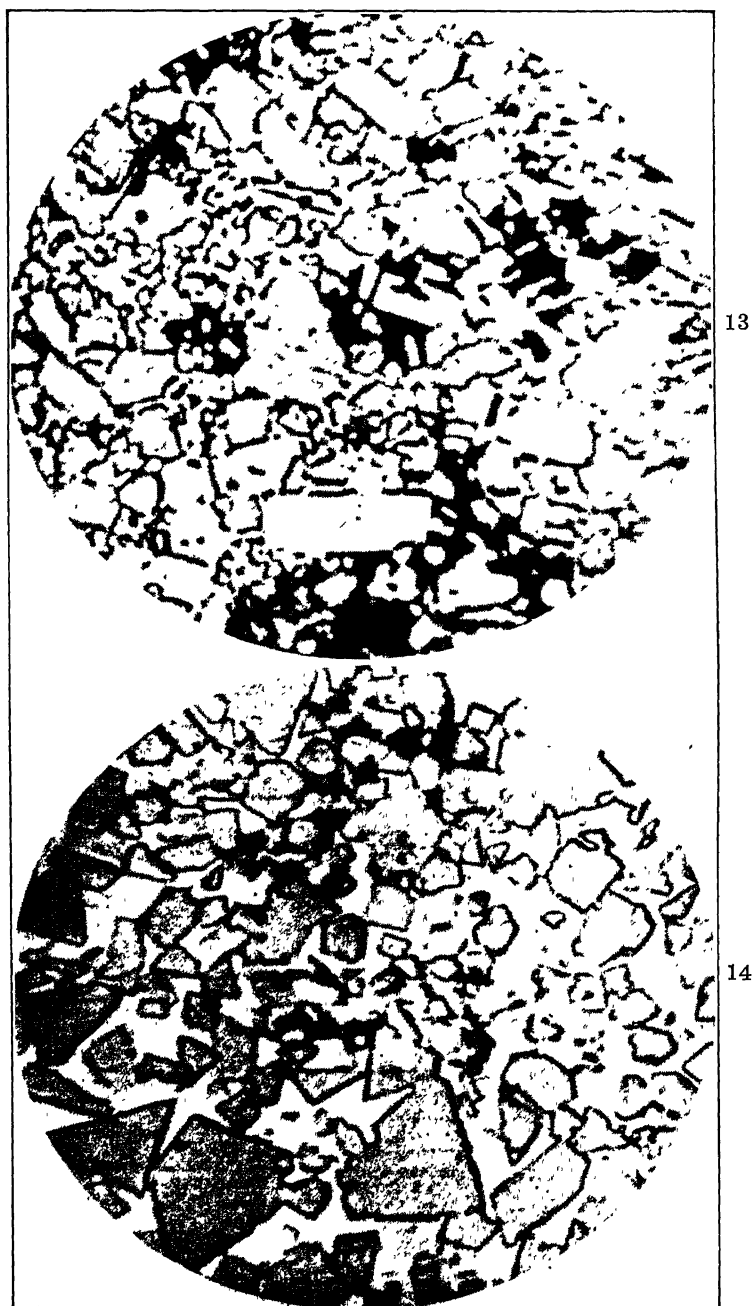
FIG. 13.—CEMENTED TUNGSTEN CARBIDE, 6 PER CENT. CO.   × 2500.
FIG. 14.—CEMENTED TUNGSTEN CARBIDE, 20 PER CENT. CO.   × 2500.

TABLE 7.—*Properties of Cemented Tungsten Carbide*

Per Cent. Cobalt	3	6	9	13	20	100
Density, grams per c.c. at 21° C ..	15 04	14.82	14.56	14.10	12.54	8 62
Rockwell A hardness, on C scale with 60-kg. load		90		87		
Vicker's Brinell number	1380[a]	1450[a]	1365[a]	1255[b]	755[b]	280[b]
Shore monotron number[c]	190	145		130		
Modulus of rupture, lb. per sq. in [d]...						
Electrical resistance, microhms per cm. cube at 20° C	21 3	21.1	22.3	19.6	29.2	9.84
Temperature coefficient of resistance, for interval 20° to 30° C....... .	0.0047	0.0045	0.0043	0.0044	0.0038	0.0036
Coefficient of expansion, average per deg. C. over interval 20° to 400° C.				6.0		

[a] 10-kg. load.
[b] 30-kg. load.
[c] Figures are the load to produce a penetration of 9/5000 in The 190 reading was for a 6 per cent. Co pressed hot, while the 145 and 130 readings were for 6 and 13 per cent. Co, but the samples were not members of this series.
[d] Transverse or cross bending test.

The test bars are either ¼ in. square or ⅜ by ½ in. cross-section. As they come from the sintering treatment they are apt to have slightly rough edges which, if left on, would lower the breaking load. Grinding
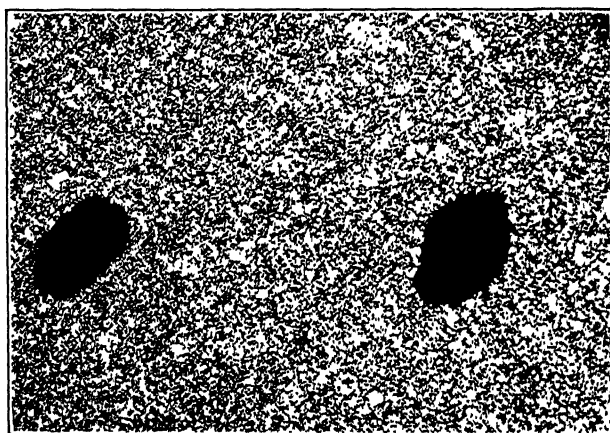
FIG. 15.—ETCHED SURFACE WITH CAVITIES.   × 240.

or lapping the surfaces flat produces more uniform results, and it is our practice to prepare test samples in this manner.

The effect of moderately elevated temperatures on the strength of cemented tungsten carbide containing 13 per cent. Co may be seen from Table 8. These are the only results of the kind that I have available

and should be read in that light.   They were obtained at the Research Laboratory on smaller bars than are usually used in this work.

TABLE 8.—*Transverse Strength at Elevated Temperatures*

TEMPERATURE, DEG. C.	MODULUS OF RUPTURE, LB. PER SQ. IN.
Room Temperature	ca. 225,000
800	183,000
850	170,000
900	141,000

These figures show a truly remarkable retention of strength at red heat and above.

Hardness

The hardness of cemented tungsten carbide is, in one sense, its most interesting property.   The hardness of the straight carbide is known to lie between that of sapphire and diamond and by some has been esti-

FIG. 16.—SAME AS FIG. 15.   × 1200.

mated as 9.8 on the Mohs scale.   The addition of the soft metal cobalt may be expected to lower this hardness in proportion to the amount added.   This is demonstrated by the relative scratch hardness of the 6 per cent. and 13 per cent. mixtures.   The former is capable of scratching

the latter without much difficulty, but, as we have seen, at the expense of some strength.

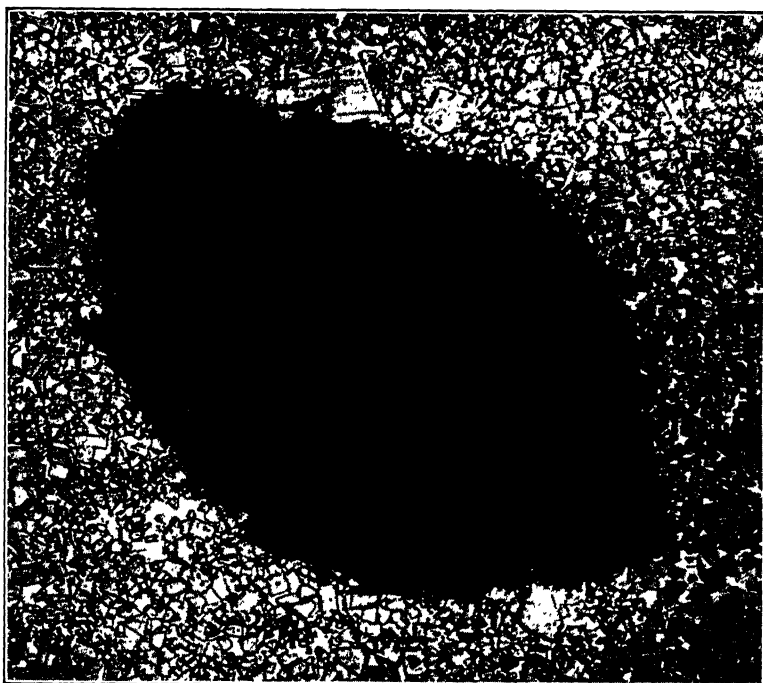The most commonly used laboratory test for the hardness of cemented tungsten carbide is the Rockwell test, although other hardness tests may conceivably be used with equal satisfaction. The standard test using the diamond cone penetrator with the 150-kg. load is seldom used, for we have found that the diamond is only too quickly broken. We generally use the 60-kg. load and take the reading off the C scale, calling the reading the Rockwell A hardness number. This lower load does not lower the specific pressure under the diamond cone, for that depends upon the "hardness" of the material tested, but the amount of the penetration is much less with the lower load and therefore the wear and tear on the diamond is less. One disadvantage of using the 60-kg. load is that the scale is contracted and the sensitivity of the test is lowered. Another disadvantage is that the work is all done on the very end of the cone, for the diamond comes to rest at a point just above the beginning of the conical portion.

Accuracy of measurement and reproducibility of readings place rather strict requirements on the accuracy with which the shape or contour of the point of the penetrator is maintained, while the high pressures involved quickly search out flaws or defects in the diamonds. It has been our experience that good diamonds give reliable results over a satisfactorily long period in both laboratory investigations and for plant control.

The Rockwell A numbers are simply arbitrary scale readings and serve only to seriate the samples according to resistance to penetration by a conical indenter. If we bear in mind that infinite hardness on this scale is 100, a better idea of the actual hardness (of this kind) is obtained. But it is more instructive to determine the actual pressure sustained by the sample and this may be accomplished by dividing the load on the diamond by the projected area of the impression and expressing the result in kilograms per square millimeter. These figures show the marked increase in hardness corresponding to a change in Rockwell A from 87 to 92, or from 1450 to 2200 kg. per square millimeter.

Fig. 17 gives the relation between the Rockwell A number and the unit pressure as calculated above. This relationship involves certain errors, concerning the shape of the cone and the measurement of the impression diameters principally, but I have found it reliable in practice. Having established this relationship, it can be used to check readings in which errors are suspected, to get the corrected Rockwell A number or to check up a new penetrator. Readings off this calibration usually are due to chipped diamonds; they may be either too high or too low. A simple examination of the diamond, or of the impression, under a binocular microscope is sufficient to reveal such a defect.

The Rockwell C number is commonly used for hard materials, hence a few determinations will be recorded here for a comparison of the C scale with the A scale. A Rockwell A number of 87 to 88 corresponds to about 69 to 71, while a Rockwell A of 92 corresponds to about 76. Some of the harder samples have given hardness numbers of 80 and above on the C scale.

It is desirable to observe certain precautions to get reliable results. While observers who are accustomed to carry out such measurements would hardly be led astray in this field, it may be worth while to set down some of our experiences here. A sample of cemented tungsten
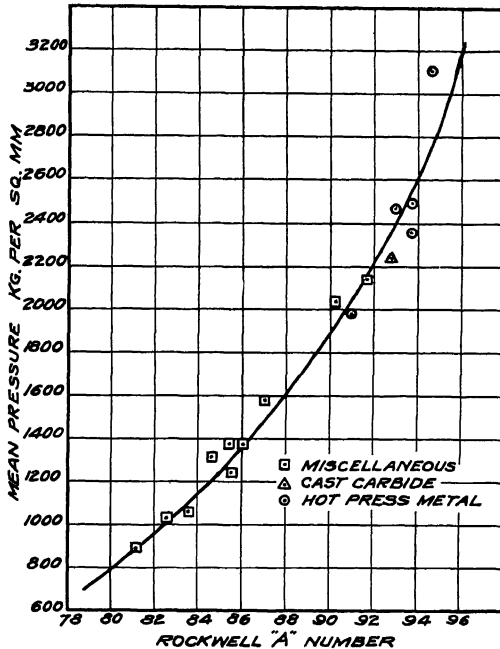
FIG. 17.—ABSOLUTE HARDNESS OF ROCKWELL A NUMBERS.

carbide ⅛ in. thick, or over, whose faces are parallel to each other and lapped or ground smooth, is in proper condition to give reliable hardness numbers. The bottom surface is almost as important as the upper surface, or the surface tested, and should be flat and free of any adherent copper or other material that might be present. The skin that may form on the surface of a heated sample gives low readings which are not representative of the inner portion, nor of the cutting edge after grinding. Unless the hardness of such a skin is desired, this surface should be ground before making the determination. Tools usually have inclined surfaces when placed on their bases. Such an inclined surface gives low readings,

while the same applies to rough surfaces, but of course for a different reason.

Hardness values determined with the Rockwell, the Shore monotron, the Vickers and the Herbert pendulum are included in Table 7 so that these figures may be recorded. Other methods of determining the hardness of these materials have undoubtedly been tried but no figures are available for inclusion here.

The Rockwell test has been used as a control of the uniformity of cemented tungsten carbide in production and as a guide in research and development work. The former use is predicated on the assumption that a standard material put through a fixed series of operations, under adequate supervision, should have certain definite properties. Possessing those properties, the behavior of the material in practice should be normal in every way, with reference to the material itself and not to the operating conditions. Such being the case, we may select the Rockwell A number and use it as a check on the uniformity of the product.

The use of the Rockwell test in research and development work has also been of great assistance, but the interpretation of the results calls for somewhat more metallurgical knowledge of the general utility of hardness tests and should be made with proper consideration for the grade of material, its cobalt content and treatment and its general properties and behavior. A loose or hasty interpretation of the figures may be not only misleading but discrediting to the test, and thus rob the experimenter of a most useful test.

Tests of the hardness at the elevated temperatures at which the material works would give interesting results, but no reliable series of figures are available at this time. We have had to work at higher temperatures and tests have been carried out at the Research Laboratory at 1000° C. and above, using a fused alumina boule with a spherical surface. The Brinell hardness numbers obtained are recorded in Table 9.

TABLE 9.—*Hardness at High Temperatures*

TEMPERATURE, DEG C.	BRINELL HARDNESS NUMBER[a]
1100	36
1300	2.7

[a] Obtained by Dr. L. Navias.

While this lecture does not contemplate the discussion of engineering problems connected with the use of cemented tungsten carbide, this section on hardness would not be adequately complete without some mention of the relation between the Rockwell hardness number and the resistance to wear or to chip abrasion. A tool of cemented tungsten carbide having a Rockwell C hardness number of 70 would normally give a very good performance, one quite characteristic of this material. This hardness number is approached by many steel samples and is even

equalled by the high-carbon tool steel reported by Sykes and Jeffries.[45] In machining operations these steels would fail utterly to approach the performance of the cemented tungsten carbide; 25 times the resistance to chip abrasion is not an uncommon superiority over tool steel. This superior performance of the cemented tungsten carbide is not even suggested by the Rockwell hardness numbers.

Density

The density of tungsten carbide may be taken as about 15.5, which is obtained from the atomic arrangement and spacing as determined by X-ray analysis and the atomic weights of tungsten and carbon. Direct measurement of the density is made difficult by the presence of voids and impurities in the material, so that the X-ray method probably yields the most reliable determinations at present. Actually there are slight amounts of impurities present. The density of cobalt may be taken as 8.7 grams per cubic centimeter.
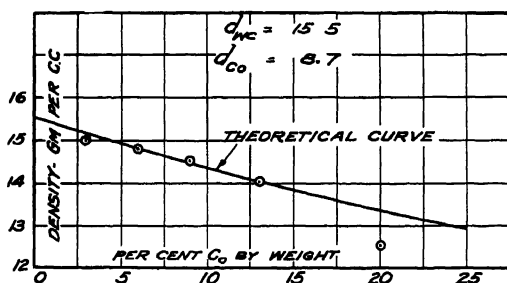
FIG. 18.—DENSITY VERSUS COBALT CONTENT.

From the known relationships connecting the densities of alloys with their compositions and the densities of their components, we may assume that the specific volume of cemented tungsten carbide will be an additive property of its constituents. This will hold unless some compound forms which differs in density from the mean of the components, WC and Co. In Fig. 18 is a plot of the theoretical density of cemented tungsten carbide of various cobalt contents on the above assumptions. The points plotted on the same figure are actual determinations made by the U. S. Bureau of Standards.

Samples of cemented tungsten carbide are known to contain voids, such as are shown in Fig. 5, although this does not necessarily represent any particular grade or product. To secure an approximate idea of the effect of voids on the density determination, I have estimated the effect of those seen in Fig. 5. If the density as determined were 14.0, the corrected density or density without voids would be 14.15.

[45] W. P. Sykes and Zay Jeffries: On the Constitution and Properties of Hardened Steel. *Trans.* Amer. Soc. Steel Treat. (1927) 12, 871.

These three properties, strength, hardness and density, are used to determine the quality of the material and to control its production.

Modulus of Elasticity

The modulus of elasticity of cemented tungsten carbide containing 13 per cent. cobalt has been determined by A. L. Kimball, of our laboratory, by measuring the natural frequency of vibration of a bar about ½ in. square by 6 in. long and calculating it from the relationship:

$$f = \frac{m^2}{2\pi l^2}\sqrt{\frac{gEI}{W}}$$

Where E = modulus; f = frequency; m = 4.73; l = length of bar; g = gravitational constant = 386; W = weight per unit length of the bar; $I = \frac{bh^3}{12}$ and b = breadth and h = depth.

The modulus was found to be 79,000,000 lb. per sq. in. with an accuracy of about 0.5 per cent.

This material has the highest modulus of elasticity of any known material and comes well above tungsten, which has a modulus of 60,000,000 lb. per sq. in. and which, in turn, has twice the modulus of steel.

I am indebted to J. V. Emmons of the Cleveland Twist Drill Co. for a determination of the torsional modulus of elasticity. In a test on cemented tungsten carbide containing 13 per cent. cobalt and high-speed steel, the former was found to have a modulus of 17,250,000 lb. per sq .in. and the latter, 8,150,000. The high-speed steel was hardened at 2350° F. after 30 sec. and drawn at 1040° F. for 30 min. The size tested in each case was 4⅜ in. long by 0.310 in. diameter.

The compressive strength of cemented tungsten carbide has been known to be rather high ever since some simple tests on this property were carried out during our early work. An actual determination of this property was first made at the Cleveland Wire Works of the General Electric Co., and found to be as high as 540,000 lb. per sq. in. in one case (Jeffries). This test marks this material as the strongest in compression of any known material. On failure, the test cubes fly into many small pieces.

The mechanical tests show that cemented tungsten carbide is an extremely stiff metal with great compressive strength and only moderate tensile strength. The design of parts which are to be highly stressed should take full account of these properties and utilize the great compressive strength as fully as possible.

Some of the more important physical properties of cemented tungsten carbide have been determined, partly at the Research Laboratory and partly at the U. S. Bureau of Standards. The results of the magnetic tests made at the latter institution are reproduced in Table 10. The bars tested at the Bureau were about ½ in. square and 7 in. long.

TABLE 10.—*Normal Induction of Cemented Tungsten Carbide*

Magnetizing Force, Gilberts per Cm	Induction, Kilo-Gauss					
	1	2	3	4	5	Cobalt
	Co, 3%	Co, 6%	Co, 9%	Co, 13%	Co, 20%	Co, 100%
100	0 19	0 25	0 38	0.58	0 90	3 35
200	0 42	0 53	0.72	1.10	1 52	5 05
300	0 60	0 81	1 05	1 50	1.95	6 20
400	0 80	1.08	1 31	1.87	2 32	7.20
500	1.00	1.31	1 58	2.17	2 68	8.00
600	1 18	1.53	1.81	2.42	2 97	8 70
700	1 35	1.77	2.03	2 67	3 25	9.35
800	1 52	1 98	2.25	2 89	3.52	9 95
900	1 70	2 17	2 45	3.10	3 78	10 53
1000	1 88	2.33	2 62	3.29	3 99	11.02

The magnetizing force of 1000 Gilberts was not enough to produce magnetic saturation and this places a serious limitation on the use of these figures for theoretical deductions. It would be particularly welcome to have figures on which calculations of the purity or composition of the cobalt cement could be based. The figures for pure cobalt were obtained on a bar made from pressed, sintered and swaged metal of the same kind as that used in the cemented tungsten carbide, and the results are included for comparative purposes.

The coefficient of thermal expansion has already been reported by P. Hidnert, of the U. S. Bureau of Standards, to the American Physical Society at the Chicago meeting on Nov. 29–30, 1929. For the 13 per cent. cobalt material, this was 6.0×10^{-6} per deg. C. over the range from 20° to 400° C. This checked and verified a previous determination which had been made at the Research Laboratory. Other results obtained at the Bureau of Standards are given in Table 7.

The thermal conductivity of cemented tungsten carbide with 13 per cent. cobalt has been determined by H. A. Robinson at the Massachusetts Institute of Technology and found to be 0.652 watts per cm. per deg. C. with a deviation of ± 0.025. This conductivity is about 50 per cent. greater than that of tool steel. The conductivities of tungsten and cobalt are given as 0.61 and 0.69 in the same units in the I.C.C.T. The electrical resistivity was also determined as 17.4 microhms per centimeter cube, as compared to 5.48 and 9.7 for tungsten and cobalt respectively. These figures show that the Wiedemann-Franz constant of cemented tungsten carbide differs greatly from that for pure metals. This constant in watts per ohm per degrees centigrade $\times 10^{-6}$ is 12.2 at room temperature, as compared to 3.3 and 6.7 for tungsten and cobalt.

Curiously, this value remains essentially constant for all conditions of sintering or over the range from 850° to 1400° C., which corresponds to a twentyfold change in the conductivities. This high value of the Wiedemann-Franz constant is due to the tungsten carbide. Tungsten carbide is relatively a much better conductor for heat than for electricity, as compared to the metallic elements.

The specific heat was also determined as 0.052 cal. per gram, which checks the theoretical value of 0.054 calculated from Kopp's rule to within 5 per cent.

Cutting Efficiency of Cemented Tungsten Carbide

I am indebted to the Metallurgical Division of the U. S. Bureau of Standards for permission to include some of the results of their determinations of the cutting efficiency of cemented tungsten carbide lathe tools containing 13 per cent. cobalt. It is intended that a more complete account of this work shall be given at a later date in a regular publication of the Bureau. These tests were made possible by a cooperative effort to which both the Bureau of Standards and the Carboloy Co. have contributed, the former by supplying the facilities for carrying out the tests (and I may add, many years of experience in this field which has added a very favorable background for the present tests), and the latter by supplying tools and material to be machined as well as advice and assistance in the conduct of the tests. This splendid cooperative effort is already yielding results of great value and will furnish users of cutting tools of cemented tungsten carbide with reliable engineering data on this new engineering material.

In these tests the laws correlating the factors which determine tool life are being studied. Fortunately, by showing that such fixed relations exist, the Bureau has already justified an extended study of all these factors and assured positive results issuing from these tests. Among the factors that have been studied are speed of cutting, depth of cut and feed per revolution. Other important factors are clearance and rake angles, contour of the cutting edge, tool size and material machined.

The test logs used were annealed $3\frac{1}{2}$ per cent. nickel-steel forgings with tensile strength of about 90,000 to 100,000 lb. per sq. in., while the tools were the Carboloy Company's standard $\frac{1}{2}$-in. by 1-in. general purpose tools ground with the usual angles for steel. In the first series of tests speeds were selected to give a tool life varying from about 10 to 150 min., while the depth of cut of $\frac{3}{16}$ in. and the feed of 0.031 in. were kept constant. Over this range the relationship between speed and tool life can be expressed within the accuracy required by these tests by the relationship.

$$VT^{\frac{1}{6}} = C = 260$$

where V is the cutting speed in feet per minute, T the tool life in minutes, and C a constant. Numerically the constant C is the speed in feet per minute at which the tool fails in one minute while the exponent of T is an expression of the effect of the speed of cutting on the change in the
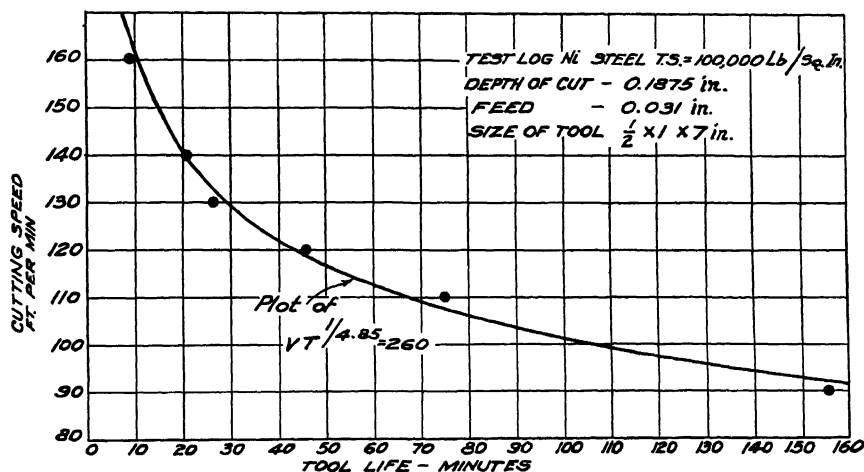
FIG. 19.—CARBOLOY TOOL LIFE.

tool life. The end point used was the moment the wear on the cutting edge had progressed so far that a small fragment chipped out and produced a glaze on the forging.

The life of the Carboloy tools is plotted in Fig. 19 against the cutting speed by the points in circles, while the relationship given above is shown
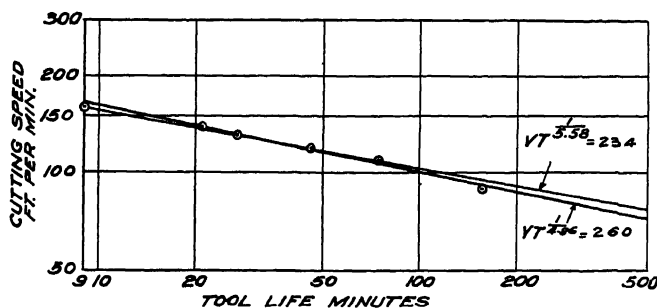
FIG. 20.—CARBOLOY TOOL LIFE.

by the graph. The "heel" of the curve comes very close to the tool life selected by Taylor, at 20 to 40 min. In Fig. 20 the same data are plotted on logarithmic paper and the straight-line relationship is observed, as with high-speed steel. A second line is also plotted, which gives preference to the higher cutting speeds.

Schlesinger has published the relative performance of high-speed steel and cemented tungsten carbide tools (Widia, in this case) in lathe tests conducted at the testing station of the Charlottenburg Technical School.[46]   A similar comparison can be made by using data secured at the Bureau of Standards.   While the test data are not sufficiently complete to enable us to draw satisfying conclusions on this point, at least one generalization can be safely made.   The cutting speeds for high-speed steel should not be increased above the "heel" because if that is done the tool enters the speed range over which the tool life falls abruptly to noneconomical values.   The introduction of the carbide tools enables us to utilize this higher range of cutting speeds for now they correspond to tool lives which are still economical.   In fact, the cutting speed has to be raised considerably before the tool life is inordinately shortened. To arrive at an approximate evolution of high-speed steel and the Carboloy tools, we may make use of the following comparison, which is given for illustrative purposes only.   A high-speed steel tool, as cited by French and Digges[47] had a "Taylor speed" (V for $T = 20$ min.) of 78 ft. per min. as compared to the 138 ft. per min. for Carboloy tool.[48]   At a cutting speed of 86 ft. per min. the high-speed steel tool would have a life of only 10 min. while the Carboloy tool would last 250 min., or 25 times as long.

Summing up, we may say that the superiority of the carbide tool becomes more marked as the severity of the cutting conditions becomes greater.   This is shown not alone by the constant C but by the larger value for the exponent of T for the Carboloy tools.

CEMENTED TUNGSTEN CARBIDE PRESSED AT ELEVATED TEMPERATURES

A study of the structure and characteristics of cemented tungsten carbide was commenced shortly after this material became available. From this study it appeared that the elimination of voids and the production of a more compact and better "knitted" structure were desirable. Methods of accomplishing these results by pressing the charge of tungsten carbide and cobalt at an elevated temperature have been worked out. This process is known familiarily as "hot-press" to distinguish it from the usual "cold-press" procedure of pressing at room temperature and subsequently sintering the pressed parts.

Tungsten carbide and cobalt are mixed by ball milling.   The mold is constructed to permit electrical heating and is provided with a top and a bottom plunger for applying the pressure.   The heating is accom-

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[46] G. Schlesinger: German Practice with Tungsten-Carbide Tools.   *Amer. Mach.* (1929) **71**, 37.

[47] H. J. French and T. G. Digges: Rough Turning with Particular Reference to the Steel Cut.   *Mech. Eng.* (1927) **49**, 339.

[48] The test log and tool size differ for these tests, so that this comparison cannot be rigid.

plished either by passing a current through the plungers, using top and bottom electrodes, or by passing current through the mold proper by using side electrodes.

The charge, as a loose powder, is placed in the mold on top of the bottom plunger and is leveled off smooth. The top plunger is inserted and the mold is placed in the press, whereupon pressure is applied to the top plunger. The heating cycle is then performed while the charge is under pressure. The pressures used range from a minimum of 1000 lb. per sq. in. to many tons per square inch, so that shrinkage occurs while the charge is under heavy pressure. This produces a thorough consolidation or packing of the particles while the formation of voids is eliminated.

The time of heating is much less than the sintering time used in the cold-press process, and may be very short. It is not likely that the pressure accelerates the rate at which cobalt dissolves tungsten carbide, although such an effect is entirely possible on account of the intimacy of contact involved, so that we may assume that a smaller amount of carbide is dissolved in the cobalt. A comparison of samples put through both processes has suggested that this may be so from the presence or retention of more of the finer grains of carbide in the hot-press material.

The hot-press process lends itself to one interesting variation, in that it is not necessary to make tungsten carbide prior to the pressing operation. E. G. Gilson has shown that a mixture of the three elements, tungsten, carbon, and cobalt, in the proper proportions produces material of the same properties and appearance as that made from tungsten carbide powder and cobalt. The conditions are such that tungsten takes up carbon rapidly.

One feature of the three-powder process may impress metallurgists who are interested in phenomena of grain growth; that is, the absorption of carbon by the tungsten in the presence of cobalt without showing any marked tendency to grow large grains. Lest I be misunderstood on this point, I do not mean to infer that such abnormal grain growth cannot or does not occur. In certain cases the particles grow to an enormous size, as compared to the usual particle size.

The temperature at which the charge is pressed is of great importance, and is controlled each time the operation is performed. This temperature also bears an interesting relationship to the pressure used, but before discussing that, a few words on the measurement of the temperature are necessary.

The use of graphite for the mold makes it possible to determine accurately the mold temperature with an optical pyrometer and thus to control the pressing temperature. But this does not give the true temperature of the charge which is inside the mold and which is not subject to the same cooling conditions as the surface. Direct measurement of the charge temperature through a small hole drilled at the center

of the mold has shown that the charge temperature may be from 150° to 200° higher than the surface temperature of the mold. Other indirect evidence points to the same conclusion.

To return to the effect of pressure, we have found that a temperature of 1350° to 1400° C. requires a pressure on the upper plunger of 1500 lb. per sq. in. and that this may be lowered, by raising the temperature, to about 1000 lb. per sq. in. A lower pressure than this, at its corresponding temperature, leaves the material in a porous condition even though the material proper has the glass-scratching hardness that characterizes standard cemented tungsten carbide. I do not mean to suggest that
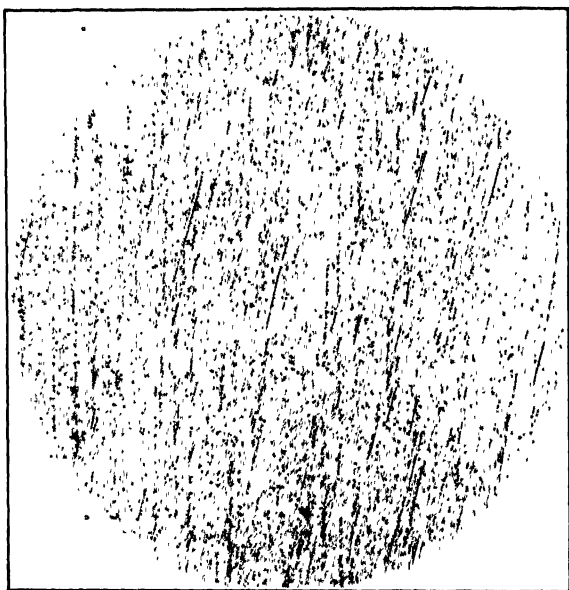
FIG. 21.—HOT-PRESS CEMENTED TUNGSTEN CARBIDE, POLISHED. × 65.

temperature and pressure are interchangeable in their effects, but it must be apparent from the results given that a balance can be struck between these two factors which will give optimum results.

The fractured surface or polished microsection of cemented tungsten carbide made by the cold-press process shows voids or cavities, as discussed above. Their appearance may be recalled by reference to Fig. 6. By comparison, Fig. 21 shows a section of cemented tungsten carbide prepared by the hot-press method. While no metal is absolutely free from defects, which may or may not show up on a polished microsection, the entirely different character of the hot-press metal will be apparent. It may reasonably be designated as free from voids and the densifying action sought may be said to be accomplished. This eliminates one feature of cemented materials which may be objectionable at times.

More specifically, the shrinkage cavities have been eliminated, as shown in Fig. 21, and this should give sound material with no voids if no other agencies or effects that would produce voids are present. Ordinarily effects of this kind are reduced to a negligible minimum by the control that is exercised over the preparation of the charge. It will probably be equally obvious that anything that would give rise to a pressure within the solid metal at local points which is greater than the applied pressure must produce a void or cavity. An examination of a considerable number of samples of the hot-press material has shown that it is consistently free from voids.

FIG. 22.—HOT-PRESS CEMENTED TUNGSTEN CARBIDE, ETCHED. × 2500.

The structure of cold-pressed cemented tungsten carbide suggests kaleidoscopic figures, which must reflect the comparatively low pressure or force that caused the packing of the particles, for the size and shape of the grains obviously have little effect on the way two adjacent grains align themselves with respect to each other. The structure of hot-pressed material shows plainly that the packing of the particles must have been produced by forces of a much greater magnitude. Fig. 22 illustrates this point.

Coming to the properties of hot-pressed carbide, it can be said in general that it has the same properties and shows the same behavior

that we have come to expect from cemented tungsten carbide, but that, other things being equal, the hot-pressed carbide is harder. This difference in hardness is shown by the Rockwell test, by greater difficulty in grinding, and by greater resistance to wear in machining or drilling operations. The strength of the hot-pressed material is likewise high and the tests that we have run show strengths consistently in the neighborhood of 275,000 to 300,000 lb. per sq. in. Incidentally, it is not a simple matter to determine the transverse modulus of rupture of hot-pressed carbide, and we do not have the same mass of information on this property that we have for the cold-pressed material.

In Fig. 17 a number of Rockwell A numbers are plotted against the absolute hardness number. The points within circles were determined on hot-press material. The highest number that has been obtained with cold-pressed material of any cobalt content is 92. This same material pressed hot, gave the absolute hardness of 3100 kg. per sq. mm., which is plotted. Its converted Rockwell A number is about 95.6.

Directed Stress in Copper Crystals[*]

By C. H. Mathewson,[†] New Haven, Conn., and Kent R. Van Horn,[‡] Cleveland, Ohio

Copper and the copper-base solid solutions readily form twin crystals when plastically deformed at a suitably elevated temperature or annealed after cold deformation. In fact, no feature of the microstructure of these materials is more prominent or characteristic than these straight-sided bands or simple lines of division which sometimes come from groups of thin polysynthetic lamellae, penetrating part way or wholly through the parent grain substance, but often divide the grain into a few or perhaps only two crystallographically related parts. Nearly always the bands as seen in the usual microscopic examination of a specimen come into vivid contrast with the adjacent crystalline material owing to the inherent difference in orientation. Bands which under special conditions of orientation cannot be seen with vertically incident light are often visible under oblique illumination and, when this fails, contrasting effects usually may be obtained by using polarized light.

There is no longer any doubt that these synthetic banded structures obtained in the ordinary course of working and annealing are due to twinning of the spinel type which was observed long ago in a number of metals crystallizing in the isometric system.[1]

It has been customary in metallurgical literature to designate these synthetic twins, which grow into prominence during an annealing process, as "annealing twins" without regard to the actual mode of their formation, which is, indeed, obscure and with scant recognition of the fact that prior deformation is essential, no twins having been observed in metal of known unstrained history. This is questionable; especially in view of the fact that in a number of metals and minerals, reorientation into the twin configuration is known to occur as a result of a simple shearing mechanism along the recognized twinning planes and the

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1 A. J. Phillips: Twinning in Copper and Brass. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 429.

C. F. Elam: An Investigation of Some Banded Structures in Metal Crystals, with an Appendix by G. I. Taylor. *Proc.* Roy. Soc. (1928) **121A**, 237.

crystallographic features of the process have been clearly written into the literature.[2] Most of the crystallographic work has been published in Germany, but recent publications of the Institute[3] contain accounts of similar studies with zinc and iron, particularly, in which X-ray methods were used successfully to verify the underlying crystallographic observations.

In scanning these results it is evident that the characteristics of twinning by deformation are variously related to the ordinary characteristics of simple deformation by slip in the different systems and this would indicate great differences in the tendency to twin when the various metals are subjected to a deforming force.

Thus the hexagonal close-packed metal, zinc, twins by shearing action along a pyramidal plane of form {10Ī2} which has never been observed as a slip plane, and the process, which requires only slight displacement of the atoms from their original positions in the lattice, occurs readily under most conditions of deformation. Only when the characteristic slip planes (0001) are favorably oriented does deformation take place by simple slip and even then twinning usually occurs before the process is concluded.[4]

Tin, crystallizing in a modified body-centered tetragonal lattice, also twins readily by deformation and here the twinning occurs along pyramidal planes of form {031} probably by shearing action with slight atomic displacements as in the case of zinc.[5] Slip on these planes has never been observed. The slip planes, according to Mark and Polanyi, are of the form {100} and {110}.[6]

Contrasting with these metals which twin so easily in what seem to be the early stages of shearing movements on parallel planes, never appearing as slip planes, is the body-centered form of iron which twins by shearing along planes of form {211}, known also to be competent slip planes,[7] and the movements both of twinning and slip proceed in the same direction [111] on these planes. In the case of slip, the movements must occur in single or multiple atomic steps so as to preserve

[2] See, for example, P. Niggli: Lehrbuch der Mineralogie, Ed. 2, 289. 1924.

[3] C. H. Mathewson and A. J. Phillips: Plastic Deformation of Coarse-grained Zinc. *Proc.* Inst. Met. Div., A. I. M. E. (1927) 143.

C. H. Mathewson: Twinning in Metals. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 7.

C. H. Mathewson and G. H. Edmunds: The Neumann Bands in Ferrite. Iron and Steel Technology in 1928, A. I. M. E. 1928 311.

[4] E. Schmid and Wassermann: Über die mechanische Zwillingsbildung von Zinkkristallen, *Ztsch. f. Physik.* (1928) **48**, 370.

[5] E. W. Roath: Twinning in Tin. M. S. Report, Yale University, 1928.

[6] H. Mark and M. Polanyi: Die Gitterstruktur, Gleitrichtungen und Gleitebenen des weissen Zinns. *Ztsch. f. Physik.* (1923) **18**, 75.

[7] See, especially, H. Gough: The Behaviour of a Single Crystal of Alpha Iron Subjected to Alternating Torsional Stresses. *Proc. Roy. Soc.* (1928) **118A**, 498.

the original orientation of the crystal. In the case of twinning, there must be a regular succession of fractional steps moving each plane along one-third of the distance between atoms in the slip direction on the next plane. Experience shows that the first of these conditions is the usual and twinning the exceptional result of deformation in this material. Twin layers form most readily, as a result of impact, in coarse-grained ferrite tending towards brittleness, and are produced sparingly in the form of very thin lamellae under the most favorable conditions.
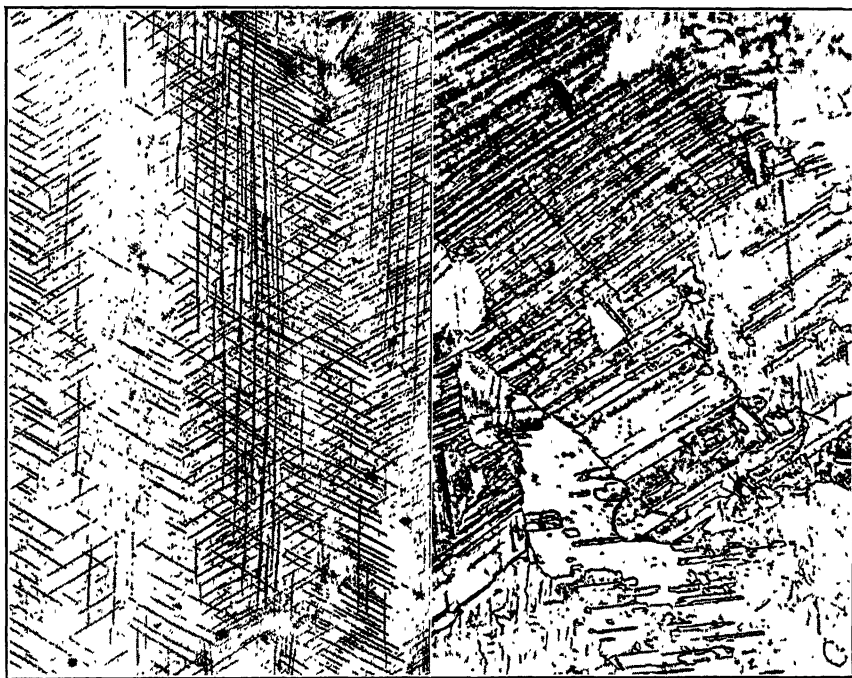
FIG. 1.—ROUGH-GROUND CASTING OF 70/30 BRASS. SURFACE AFTER POLISHING AND ETCHING.

FIG. 2.—ROUGH-GROUND CASTING OF 70/30 BRASS ANNEALED AT 400°. SURFACE AFTER POLISHING AND ETCHING.

In line with these pronounced differences in the mode of formation and the dimensional restrictions of deformational twins in different metals, we might expect great differences in the stability of the twin layers on heating due to the prevailing condition of constrained or unconstrained atom packing at the boundaries.

Thus, in a generally deformed structure, straight twin boundaries might be obliterated by irregular growth or, on the contrary, might serve as stable nuclei for further growth or extension resulting in the familiar coarse twin crystals of the alpha copper solutions.

In an elaborate and instructive series of metallographic studies, A. J. Phillips[8] has sought to trace the connection between the etch markings (Fig. 1), reminiscent of Neumann bands, produced by rough-grinding cast samples of brass or bronze and the twin bands developed on annealing. Both etch markings and bands are always found parallel to the traces of octahedral planes on the surface of the crystal examined and frequently, after annealing at a temperature just high enough to produce recognizable bands, it can be seen that these seem to form directly from
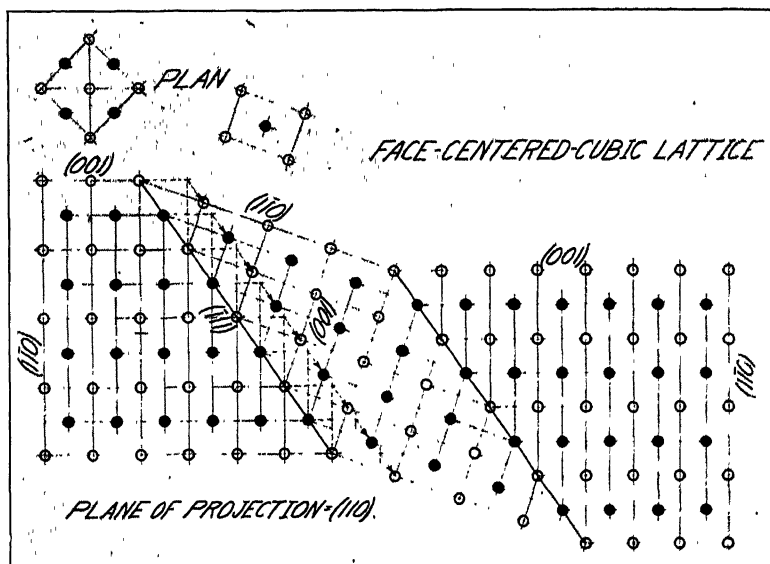
FIG. 3.—ATOMIC ARRANGEMENT THROUGH A TWIN BAND IN THE FACE-CENTERED CUBIC LATTICE.

parts of the deformational bands. However, general deformation evident from the curvature of the markings obviously complicates the process by introducing general features of recrystallization. The transition from deformational markings to annealing bands may be seen in Fig. 2 which represents a sample of 70/30 brass rough-ground and annealed at 400° C. It is thought that many of the deformational lamellae are absorbed by the original crystal, while others develop into annealing bands.

The shearing process (*einfache Schiebung*) along octahedral planes, which would result in twin lamellae of the crystallographic characteristics actually encountered in copper and the copper-base solutions, is illustrated in Fig. 3, originally drawn by A. J. Phillips[8] for the purpose

[8] A. J. Phillips: Twinning in Relation to the Plastic Deformation of Metals. Dissertation, Yale University, 1928.

of indicating the atom displacements necessary to produce this form of reorientation.

The movements from plane to plane are one-third of a full step between atoms in the direction of shear, as previously stated for iron. The twinning plane, of form {111}, is also a competent slip plane; in fact, the only form of plane definitely observed as a slip plane in the face-centered cubic lattice. However, the process outlined differs considerably from the process observed in iron,[9] in that the required direction of shear on the octahedral twinning plane is not in the direction of a line of closest atom packing [110], but in a direction [112] halfway between two such lines. This is the form of movement naturally taken by balls piled on one another in the close-packed {111} arrangement, when tilted and allowed to roll under the influence of gravity. This is probably a fact of only passing significance, as it does not take into account the forces between atoms in various directions.

An understanding of the origin of the twin formations, which are so common in the microstructure of copper and its alloys, is of great importance, inasmuch as this relates fundamentally to the inner structure of these alloys and should not be overlooked in evaluating their properties. The authors planned, therefore, to determine whether the simple form of mechanical twinning, illustrated in Fig. 3, could be effected by deforming blocks cut from single crystals of copper with a maximum stress intensity in the direction indicated [112] on favorably located octahedral {111} planes.

It was apparent at the outset, from the fundamental work of Professor Taylor and Dr. Elam[10] on the process of deformation in tension loading of aluminum crystals and the subsequent work of Dr. Elam[11] on copper crystals, that the natural, unrestrained tendency would be for slipping to occur on a favored octahedral plane in a favored [110] direction. Taylor and Elam gave a thorough mathematical analysis of the distortion suffered by lines ruled on the sides of the single-crystal aluminum test pieces and determined the relation between the axis of the test piece and the crystal axes, from time to time during extension, by X-ray measurements. They made many experiments with crystals of different orientation and were able from stress considerations to chart all possible orientations on a stereographic diagram and predict therefrom the plane and direction (corresponding to maximum stress intensity) which would initiate the slipping process. The work with copper was not done

[9] C. H. Mathewson and G. H. Edmunds: *Op. cit.*

[10] G. I. Taylor and C. F. Elam: Plastic Extension and Fracture of Aluminum Crystals. *Proc. Roy. Soc.* (1925) **108A**, 28.

[11] C. F. Elam: Tensile Tests of Large Gold, Silver and Copper Crystals, *Proc. Roy. Soc.* (1926) **112A**, 289.

in such detail, but from tension tests and X-ray determinations on a few crystals an analogous behavior was predicted.

It was therefore considered essential in the work described here to choose a method of deformation that would tend to direct the slip in the desired direction and restrain it from proceeding in the direction of least resistance. This was attempted by squeezing the specimen between the jaws of a specially constructed vise with the hope that the frictional gripping effect of these jaws might guide the deformation as desired. Thus in Fig. 3 the jaws might be located at the top and bottom of the (undeformed) structure shown and a diagonal compressive force exerted in the desired direction. Later, supporting members were introduced at the sides in a further effort to prevent slip on the (111) plane shown from proceeding out of the plane of the drawing towards the front or the rear in one or the other of the preferred directions.

PREPARATION OF SINGLE CRYSTALS

Following the method used successfully by Elam[13] and others, copper crystals large enough for experimental purposes were made by slowly passing a crucible charge of metal through the heating zone of a suitable furnace. In the authors' experiments, an Ajax-Northrup 35-kva. converter supplied energy to a furnace consisting of a water-cooled primary coil of about 50 turns of flattened copper tubing shaped to fit closely around the central 9 in. of a silica tube 12 in. long and about $3\frac{1}{2}$ in. dia. A long alundum tube of $1\frac{7}{8}$-in. bore was used inside this silica tube and the intervening space was filled with insulating material to prevent air currents. An outside shell with top and bottom plates served to house the heating unit. The crucible, merely a length of drilled carbon rod, was lowered at uniform speed through the alundum furnace tube by means of a clock mechanism, which consisted of a protruding shaft and drum attached to the minute hand of a sturdy clock. Fine nichrome wire was wound around the drum and attached to a wire basket support fashioned around the crucible.

Illuminating gas was passed up through the alundum furnace tube and sufficient air was admitted at the bottom to prevent the excessive deposition of soot from decomposing hydrocarbons in the hottest part of the tube.

Cathode copper of highest purity (99.99) was used in most of the work. It was melted and solidified under the conditions described without any evidence of oxidation.

A furnace of this kind operates by inductive heating in the conducting material used; hence the size and composition of the carbon container, as well as the kind and amount of metal used, affect the results. At first,

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[13] C. F. Elam: *Op. cit., Proc.* Roy. Soc. (1926) **112A**.

carbon electrodes from ordinary dry cells were used for crucible material, but, probably on account of the variable amounts of the different carbonaceous materials used in them, variable heating effects were obtained and Acheson graphite was finally used instead.

The inductive stirring effect in the melted material usually urged as an advantage in this kind of heating was not observed and indeed it seems doubtful whether single crystals could be successfully grown in a metal continuously subjected to agitation. Under the conditions of these experiments, in which only a few ounces of metal were melted, the attainable heat was found to depend principally on the amount of graphite in the secondary.

At first a $\frac{1}{2}$-in. bore was used for the crucible, then a $\frac{1}{4}$-in. bore and finally, in most of the experiments, a $\frac{3}{8}$-in. hole tapered at the extremity in order to favor the starting of a single crystal at the point. It was found expedient to bore four holes in a single rod and grow four crystals at once. Precautions were taken to ensure a smooth and uniform inner surface of the crucible, as dirt, graphite protuberances or oxide might be expected to act as centers of crystallization.

The best speed of lowering the crucible or mold was determined by trial. Different speeds were obtained by varying the drum size. Speeds of 1.5, 1.18, 0.78, 0.62, and 0.48 in. per hour were tried and resulted in consistent increases in crystal size. The last speed was the minimum attainable with the minute hand of the clock, so the mechanism was reconstructed to operate on the hour hand (one complete revolution in 12 hr.). Speeds of 0.33 and 0.24 in. per hour were then obtained with drums 1 in. dia. and $1\frac{1}{2}$ in. dia., respectively. The latter speed proved very satisfactory for the multiple production of copper single crystals. At this speed, 14 hr. were required to lower through the hot zone of the furnace a 6-in. graphite cylinder of $1\frac{1}{4}$ in. dia., containing copper in four $\frac{3}{8}$-in. tapered holes. These conditions apparently represent a suitable relationship between the volume of metal and speed of crystallization.

Great care was necessary in removing the crystals from the mold. Generally, they could be dislodged without serious deformation. In difficult cases, the removal could be facilitated by liberal application of mineral oil.

In the preliminary work the specimens were metallographically polished, etched and examined to determine their condition; but later ordinary visual examination without magnification, after pickling in concentrated nitric acid, was found to be sufficient for this purpose. Generally two, of a possible four, single-crystal copper pencils 5 to 6 in. long, could be produced daily. On one occasion, four single crystals were obtained. After the best conditions has been ascertained, about two dozen satisfactory crystals were secured during the course of a two weeks' campaign.

To summarize, it appears that the production of single crystals is largely a matter of mere chance, even assuming the presence of favorable experimental conditions. If the grain most favorable for growth starts at the bottom, it continues to impress its orientation on the remainder of the melt. If a grain less favorable to grain growth is initiated at the bottom, it is likely to be replaced by a preferred grain, and so on until the grain most favorable for grain growth is formed, which will then continue to grow until the melt is exhausted. Under favorable conditions, there appears to be an even chance for the immediate formation of a preferred grain. Additional precautions, such as tapered ends, uniform sides, etc., do not appear to have any material influence if a favorable grain starts automatically at the beginning of the process.

METHOD OF CUTTING SECTIONS ON PREDETERMINED PLANES

The proposed plan of investigation calls for the deformation under controlled conditions of thin slices of metal cut from the single-crystal pencils along predetermined crystallographic planes. One requirement was for a single-crystal specimen in the form of a narrow, rectangular prism bounded by planes of form {112}, {110} and {111}.

These specimens were cut in a device resembling the familiar miter box used in woodcraft. The first crystallographic reference plane, of form {111}, was located by producing slip bands on the two flat sides of a section cut across the single-crystal pencil, which had previously been milled flat on one side to produce a convenient plane of reference parallel to the axis of the pencil.

In order to cut along a selected plane in a cylinder it would be necessary to have two rotations; for example, one about a horizontal axis and the other about a vertical axis. Rotation about a horizontal axis normal to this first horizontal axis might be substituted for rotation about the vertical axis. The ordinary miter box utilized in woodcraft possesses a saw blade capable of rotation in a horizontal plane. If the crystal were fixed in a definite position, only the planes that happened to be exactly vertical in the cylinder could be cut by moving the blade into different positions. The necessity of a second rotation is obvious and this could be accomplished in two ways. The first way would be to move the saw blade about a horizontal axis, as well as about the original vertical axis, and the second, to rotate the crystal itself in a suitable holder about a fixed horizontal axis which would preferably coincide with its own major axis. The latter possibility appeared to be the most practical and a device called a goniometric miter box was designed on this principle.

This device (Fig. 4) consists essentially of three parts: a base plate, a movable saw and a crystal holder. The front of the base plate is machined in semicircular form and fitted with a 4½-in. protractor at the

center of which is the vertical axis of rotation of a frame carrying two slotted steel uprights for guiding the motion of the saw. The back of the base plate is rectangular in shape and possesses a slot extending nearly half its length, for attachment of the crystal holder. One end is rigidly bolted to a steel block, which can be clamped in a vise or other arrangement for holding the device firmly when in use.

A special saw blade, 0.013 in. thick, fits into two precisely machined slots in the two steel uprights of the saw frame. The width of the slots is only 0.002 in. greater than the thickness of the saw blades. This precaution was taken to ensure a rigid support for the midget saw frame and to prevent any lateral play of the blade. The extremity of the steel bar carrying the uprights is attached to one end of the brass arm which
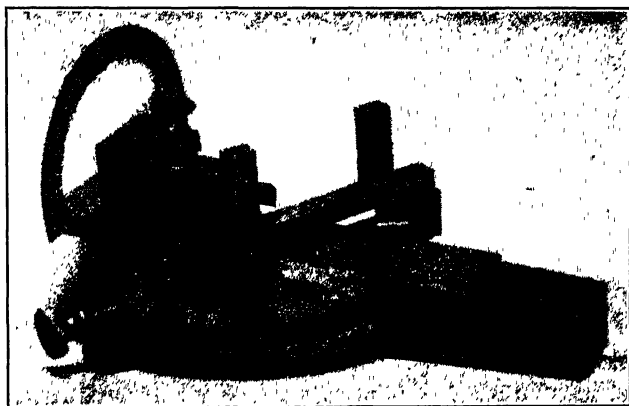
FIG. 4.—GONIOMETRIC MITER BOX.

pivots at the center of the protractor or semi-circle. This arm extends underneath the base plate and is furnished with a sturdy thumb screw and pointer at the other end; thus the saw can be rotated to any point on the semicircle and securely fastened, and the amount of rotation can be read on the protractor attached to the base.

A $\frac{3}{4}$-in. brass bushing with a $\frac{3}{8}$-in. hole serves as the crystal holder. The crystal is fastened in the bushing by three countersunk set screws. A vertical reference mark was placed on the end of the bushing adjacent to the saw and a corresponding reference mark scratched on the specimen to serve as a guide in resetting the crystal. The bushing rests on a sliding base, which moves in a slot in the main base plate and can be fastened by a large thumb screw. It is attached to this sliding base by means of a V-shaped yoke and two screws. The end of the sliding base is fitted with a protractor, and a suitable pointer is soldered to the end of the bushing. By this means the crystal bushing can be rotated to any position, fastened, and the amount of rotation read on the vertical protractor.

In using this device, plenty of time was taken to make a cut and great care was used to avoid bending the crystals.

LOCATION OF AN OCTAHEDRAL PLANE

One of the copper single-crystal pencils was selected and carefully re-etched with concentrated nitric acid in order to detect the possible occurrence of small crystal grains, which would have to be avoided in the subsequent adjustments. A flat surface was made on the crystal by careful planing followed by polishing to remove the effects of distortion. It was then placed in the crystal holder of the miter box and rotated until
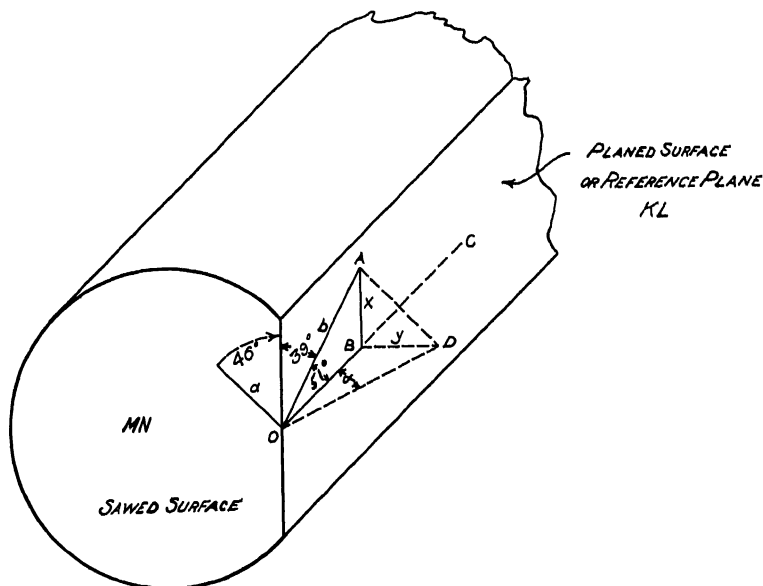
FIG. 5.—METHOD FOR LOCATION OF AN OCTAHEDRAL PLANE.

the plane surface of reference became vertical. The saw was thereupon rotated to the 90° point on the horizontal protractor and a test specimen cut at right angles to the long axis of the pencil. This specimen therefore possessed two boundary planes normal to each other.

Both of these surfaces were carefully polished and the specimen was squeezed in a vise to produce slip markings on both surfaces. It was desired to find the traces of the same octahedral plane on the two prepared surfaces; in other words, to trace slip bands from one surface over the edge on to the other surface.

This was not usually difficult. Fig. 5 represents the traces of such a slip plane on both surfaces, with indication of the angles between the respective traces and the line of intersection of the reference planes. The recorded angles were mean values obtained from measurements on 11

parallel slip bands. If the crystal is then rotated 46° in a clockwise direction, the trace a of the octahedral plane on the sawed surface MN will become vertical. With the octahedral plane vertical it is now desired to calculate the position of the trace b in a horizontal plane, which is, of course, the required position of the saw blade in the horizontal plane for a cut parallel to the (vertical) octahedral plane. This horizontal angle is calculated by means of three triangles which are represented in Fig. 5. The first is a right triangle AOB determined by the trace b, and a line x drawn vertically from a point on trace b so as to intersect a unit distance OB on the line OBC, which lies in an element of the plane surface KL drawn through the point O parallel to the intersection of the cylinder surface with the plane KL.

The second triangle cannot be conveniently shown in Fig. 5; it is a triangle ADB after clockwise rotation of 46° to bring trace a in a vertical position in which the angle ADB becomes a right angle, the line x the hypotenuse, AD a vertical line from point A in its new location to the horizontal plane, and y a line in the horizontal plane as shown between B and D. The angle BAD corresponds to the angle of rotation.

The third right triangle is in the horizontal plane; it is composed of the unit distance OB, the line y and the trace of the octahedral plane OD. The desired angle α of the trace OD in the horizontal plane, therefore, can be calculated from these relationships in the following manner:

$$\tan 51° = \frac{x}{1} = 1.234$$

$$\sin 46° = \frac{y}{x} = 0.719$$

$$y = 0.885$$

$$\tan \alpha = \frac{y}{1}$$

$$\alpha = 41° \; 30'$$

This angle would be measured clockwise from the horizontal axis of the specimen.

Accordingly, a thin section of metal was cut after rotating the crystal 46° about the horizontal axis and the saw 41° 30′ about the vertical axis. It was found that 0.040 in. was the minimum thickness that could be cut without producing unavoidable distortion. The part of the crystal extending out of the crystal holder was firmly supported by a metal block, to avoid bending due to pressure of the saw. As a general rule, the cutting of one of these elliptical sections consumed from 30 to 45 minutes.

In order to test the accuracy of the mechanical work in preparing crystallographic sections through the single-crystal pencils and to deter-

mine significant directions in the exposed plane, these specimens were examined by X-rays.
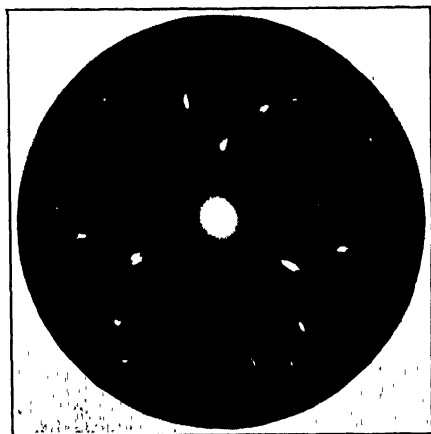
FIG. 6.—LAUE PATTERN TAKEN IN A DIRECTION NORMAL TO CALCULATED OCTAHEDRAL PLANE.

Careful polishing was first necessary for the purpose of eliminating saw marks and this was followed by dipping in concentrated nitric acid for short intervals with subsequent washing until a thickness of 0.010 to 0.015 in., favorable to the X-ray work, was attained.

All specimens for X-ray examination were mounted over pinholes, 0.02 in. square, of a multiple diffraction apparatus (General Electric Co.) containing a Coolidge tube with molybdenum target operating at 30,000 volts and 25 milliamperes. The specimens
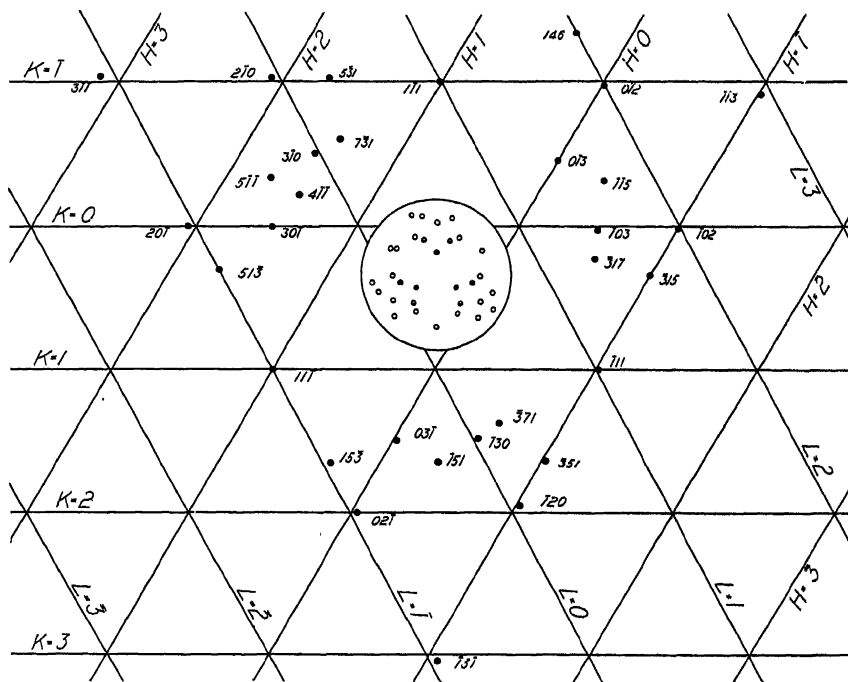
FIG. 7.—GNOMONIC PROJECTION OF REFLECTING PLANES REPRESENTED IN FIG. 6.

were exposed from 12 to 36 hr. to general radiation from the molybdenum target directed normally to the prepared plane surface.

The pattern obtained from the crystal section cut along an octahedral plane according to the previous description is shown in Fig. 6. Threefold symmetry, characteristic of this orientation, is clearly evident. A gnomonic chart is given in Fig. 7. In this chart the Laue reflections are shown within the circle at the center as full shaded circles representing reflections of high intensity, half shaded circles for reflections of medium intensity, and hollow circles for reflections of low intensity. The gno-

$\bigcirc$ = POSITION OF REFLECTION ON X-RAY PATTERN

$\square$ STEREOGRAPHIC PROJECTION OF REFLECTING PLANE
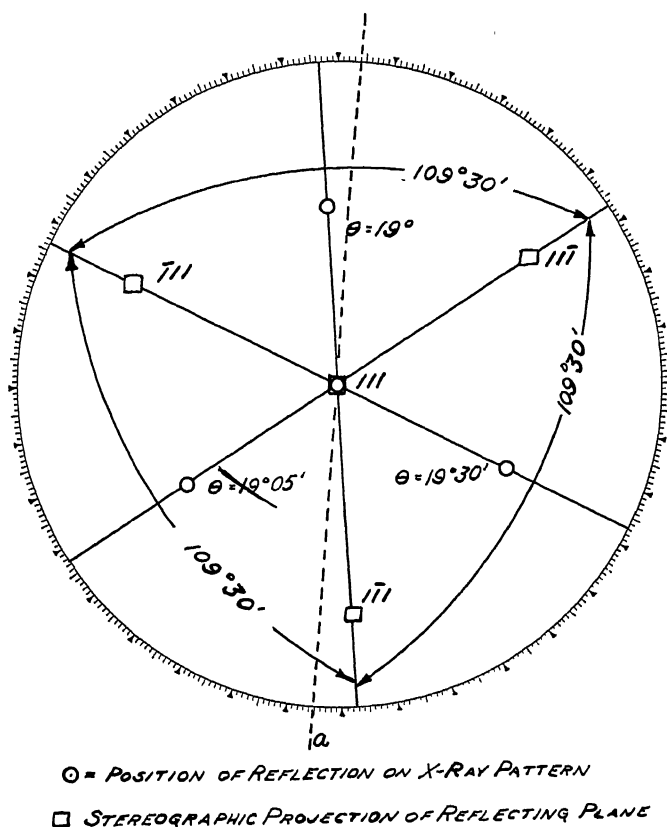
FIG. 8.—STEREOGRAPHIC PROJECTION OF OCTAHEDRAL PLANES REPRESENTED IN FIG. 7.

monic projections of the reflecting planes are represented by the full shaded circles in the outlying regions of the chart. The indices of the reflecting planes can be determined from the network, the meshes of which are almost perfect equilateral triangles, indicating only a slight deviation of the octahedral plane from a position exactly normal to the beam. This deviation can best be determined by constructing a stereographic projection of the strongly reflecting planes of form {111} and measuring the included angles with a Wolf net. Fig. 8 shows the result of this process, from which it appears that all of these angles in the present

case are approximately 109° 30', indicating only a slight deviation of the octahedral plane from its calculated position, well within the ordinary errors of manipulation and plotting. The dotted line through this chart locates the trace of the reference plane (*KL* of Fig. 5) in the octahedral plane section cut through the crystal.

LOCATION OF A DODECAHEDRAL PLANE

A section parallel to a dodecahedral plane was cut through the single-crystal pencil after an adjustment in the miter box determined from the stereographic chart shown in Fig. 9. The rotations previously
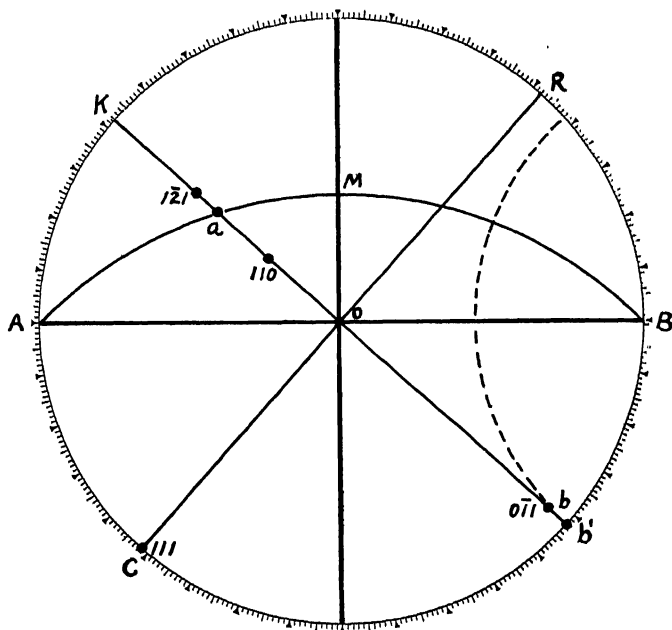
FIG. 9.—STEREOGRAPHIC METHOD FOR DETERMINATION OF A DODECAHEDRAL PLANE.

described for cutting an octahedral plane give the starting point for this construction. *AB* represents the horizontal axis of the specimen and the upper half of the fundamental circle is used to represent the rotation of the saw blade in the horizontal plane. The saw cut was made along the line *KO* (41° 30' from *A*), which is the trace of the octahedral plane (111) with pole at *C*. The great circle *AMB* is a projection of the intersection of the reference plane (*KL* of Fig. 5) with the primitive sphere and *a*, the intersection of this reference plane with the octahedral plane. The stereographic chart given in Fig. 8 shows that this intersection *a* is only 8° from the nearly vertical line representing a [112] direction or 38° from a [110] direction on one side and 22° from a similar direction on the other side. These angles were measured in the zone *KO* and

located as shown in the chart. It is observed that the pole of a dode-cahedral plane ($0\bar{1}1$) lies close to the primitive circle; *i. e.*, this plane is in a nearly vertical position. The operation was therefore completed by rotating the crystal 5° around its axis AB, bringing this plane into verti-cal position with pole at b' and finally rotating the saw to cut in the direction OR. Satisfactory crystal sections parallel to a dodecahedral plane, for the experiments to be described later on, were prepared in this way and checked for orientation by X-ray analysis.

The Laue pattern and gnomonic projection practically unchanged after a small amount of deformation are shown in Figs. 16 and 17, respectively.

Other sections were prepared and checked by similar methods, for the rolling experiments on cubic planes.
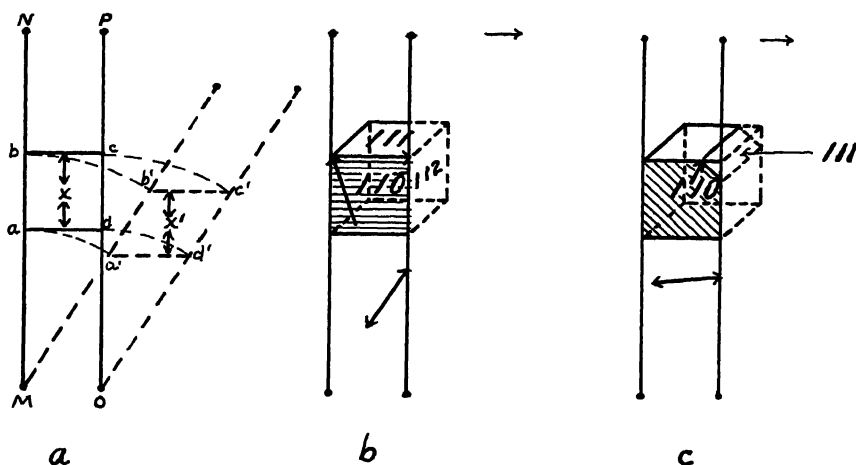
FIG. 10.—METHOD OF DEFORMING CRYSTAL SECTIONS.

DEFORMATION OF ORIENTED SECTIONS

The principal undertaking in these experiments was to carry out a process of deformation on properly oriented sections cut from single crystals which would imitate the conditions represented in Fig. 3. These obviously correspond to pure shear with the twinning plane stationary and superimposed planes suffering amounts of parallel displacement that are proportional to their distance from the base plane.

After some consideration it was decided to construct a vise with jaws pivoted at the extremities MN and OP as represented in Fig. 10a. Moving towards the right, a rectangular area $abcd$ between these jaws changes to a rhomb $a'b'c'd'$ and this to represent pure shear would have to occur by parallel displacement of horizontal planes. There is, however, a decrease in the altitude and therefore in the area of the space bounded by

the jaws so that a specimen undergoing shear must slip in the jaws to avoid this compression.

The friction between jaws and specimen would depend on a number of factors, among them the fit or smoothness of the surfaces concerned, the use of lubricants, etc. As it is not possible accurately to resolve the stresses concerned, it cannot be foretold to what extent the deformation will occur by displacement along diagonal planes or by combinations of slip on various planes parallel to the axis of rotation of the jaws.

FIG. 11.—STEREOGRAPHIC PROJECTION OF IMPORTANT PLANES IN ISOMETRIC SYSTEM. PLANE OF PROJECTION (011).

In the experimental work, a variety of conditions in this respect were realized by placing the specimen between the jaws of the vise in each of the two positions, 10b and 10c. In the first position, the two octahedral planes eligible for twinning movements in the plane of the drawing (perpendicular to the axis of rotation) are (1) horizontal and (2) inclined 20° to the vertical, while in the second the planes are inclined (1) 40° and (2) 30° to the vertical. The directions of shear necessary for twinning according to the basic scheme of Fig. 3 are indicated by arrows.

Information concerning the location of other planes may be taken from the stereographic chart Fig. 11 of planes in this system projected

in the dodecahedral plane. Thus, it is apparent that in Fig. 10b the other two sets of octahedral planes are equally inclined (35°) to the dodecahedral plane shown on the drawing and have a common direction of slip in this plane inclined 35° to the vertical (indicated by the lower arrow). The corresponding angle in Fig. 10c is 85°.

A photograph of the special form of vise devised for these experiments is shown in Fig. 12; it consists of two polished parallel jaws, A and B, each of which pivots on pins whose centers are in the same plane as the face of the jaw. The pins belonging to jaw B are attached at K and L to two jaw supports C and D, which are permanently fixed to the heavy
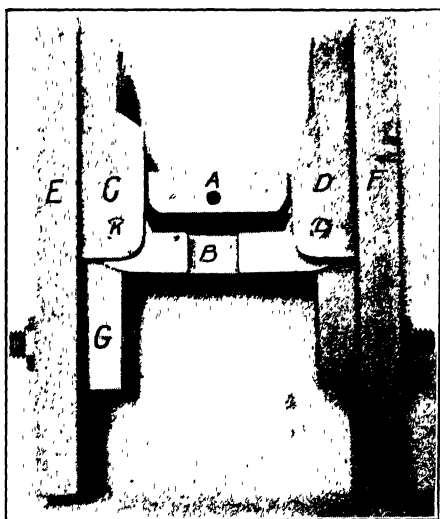
FIG. 12.—DEVICE FOR DEFORMING ORIENTED CRYSTAL SECTIONS.

FIG. 13.—THIN SPECIMEN AFTER DEFORMATION.

side plates E and F. The pins belonging to jaw A, hidden by the members C and D, are attached to the two jaw supports G and H, which move in slots in the side plates and permit displacement of the jaw to accomodate specimens of different size. After adjustment the jaw can be clamped in the desired position by means of the two bolts extending through the side plates. The device is operated by moving the side plates in opposite directions and the angle of rotation can be read by means of a protractor adjusted to a reference mark extending through the center of one of the pivot pins.

In the first group of experiments a number of specimens of different dimensions were oriented between the jaws of the vise as shown in Fig. 10b. The adjustment of thin specimens perpendicular to the jaws was

facilitated by using a brass guiding block, which was removed after clamping the jaws on the specimen. These thin specimens invariably buckled when the pressure became considerable in rotating the jaws of the vise. The appearance of the dodecahedral face of a specimen rotated 26° is represented in Fig. 13. Horizontal as well as diagonal slip bands along planes inclined about 35° to the vertical are visible but the principal markings are in the nature of elevations and depressions where the specimen has crumpled under pressure.

Deformational Bands in Unequally Strained Parts of a Single Crystal

This specimen was ground to a flat surface, polished, etched in a mixture of ammonium hydroxide and hydrogen peroxide and photo-
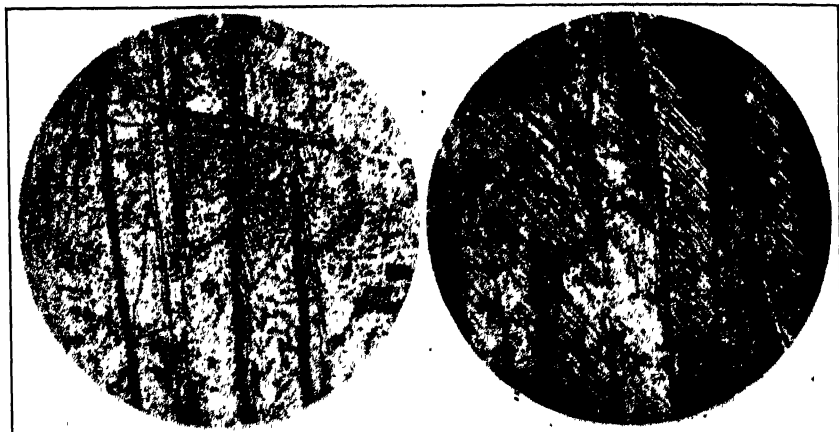
FIG. 14.—SPECIMEN SHOWN IN FIG. 13.   FIG. 15.—CHANGE OF DIRECTION OF SLIP
× 100.   MARKINGS IN PASSING FROM ONE DEFORMA-
TIONAL BAND TO ANOTHER.   × 100.

graphed (Fig. 14). The tapered, spindlelike bands closely resembling mechanical twin bands in zinc or tin lie in an approximately vertical position and seem to match the folds seen on the original dodecahedral surface.

From the stereographic projection of important planes on a dodecahedral surface, given in Fig. 11, it is apparent that the observed deformational bands do not lie parallel to the trace of any octahedral plane. As twinning is known to follow the octahedral planes in copper, it was concluded that the present markings could not represent mechanical twin lamellae but must be deformational bands of some other kind.

Geometrical markings, not unlike these, formed in the early stages of plastic deformation in iron and steel, have long been recognized under the name "Lüders lines." These have been fully described by Hartmann, Fremont, and Howe. The most recent work on this subject is by Raw-

don,[14] who discusses the earlier work in this field and seeks to clear up obscure points by carefully examining these effects in mild steel and aluminum, with the aid of modern methods of testing, including X-rays.

Hartmann demonstrated that the Lüders lines lie at a constant angle to the direction of maximum stress intensity. If a polished tensile-test bar is strained by gradual application of a load, no change will be noticed until the elastic limit is attained; then there appears across the bar an oblique marking, which is a constriction along a plane that generally makes an angle of 60° with the axis of the bar. As the stress is increased the original band widens and more parallel or conjugate bands occur. Each band represents a permanent set and definite necking occurs where the constrictions are most prevalent. He observed similar markings 55° to 65° to the direction of applied stress in compressed steel sheets.

Howe observed Lüders lines at certain angles determined by the stress distribution and also noticed markings normal to the axis of tension in parts of a tensile specimen located near the grips. At this point the stress would not be as evenly distributed as in the central section. He shows that even wood, if compressed parallel to its fiber, "may yield by shearing along the lines of Lüders at an angle of about 65° with that fiber, in spite of its weakness along the fiber as shown by its ready splitting under the ax."

Howe defined Lüders lines as depressions or constrictions in the surface and attributes their occurrence at various angles to the fact that the metal in these locations "offers its least resistance to a combination, in a certain specific ratio, of a direct pull or push with a shearing stress." This is called the most effective stress ratio.

The Lüders bands are often called, in a general way, "displaced orientations." In the present case, slip bands could easily be made to traverse the bands by simple straining in a vise. The result shown in Fig. 15 indicates an abrupt, although slight, change in orientation from band to band. The bands evidently represent separate areas of approximately uniform deformational origin adjusted to one another on the basis of stress characteristics or peculiarities but not according to any specific crystallographic plan of attachment.

X-ray exposures taken perpendicular to the (110) plane in which these foldings were observed gave highly asterized or striated patterns, which could not be analyzed and in which not even the symmetry of a dodecahedral surface could be recognized. From a qualitative point of view it may be said that the films all showed a number of similar reflections but that a few intense spots were missing on some diagrams which were present on others. This lack of consistency, of course, corresponds to differ-

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, [14] H. S. Rawdon: Strain Markings in Mild Steel under Tension. U. S. Bur. Stds. *Jnl. of Research* (1928) 1, 467.

ences of orientation due to displacement along the specific paths indicated by the foldings in the specimen.

Specimens deformed under the influence of complex stress, revealed by these banded structures, recrystallized on annealing with the formation of twin bands which, owing to the irregular distortion of the specimen, could not be related to any definite octahedral plane.

By changing the dimensions of the specimen so that the surfaces bearing on the jaws of the vise were large in comparison to the exposed octahedral (top and bottom) and dodecahedral (front and back) surfaces large amounts of deformation could be effected without sidewise distortion. These specimens showed both horizontal and diagonal slip bands at the sides, evidently the traces of octahedral planes represented in Fig. 10b. Slip in directions parallel to the front (110) plane on which observations were made obviously should not be visible in this plane but doubtless very small errors in the cutting of these sections would be sufficient to change this condition.
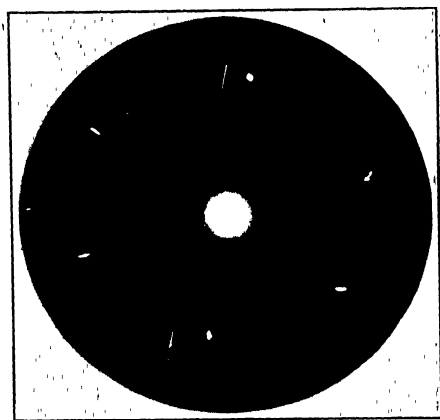
FIG. 16.—DIFFRACTION PATTERN OF A SINGLE CRYSTAL SPECIMEN DEFORMED 5 PER CENT.

Twin lamellae of appreciable dimensions, if formed, should be visible on such a surface after polishing and etching, and the entire absence of such markings seems to prove that the movements on the octahedral planes were in the established [110] directions, which would make them 30° sidewise movements on the horizontal and diagonal planes indicated in the cube of Fig. 10b, but movements exactly in the front vertical plane (of observation) in the case of the diagonal planes whose common trace is shown below the cube.

From the prevalence of diagonal markings, it was decided to mount specimens between the jaws in the position shown in Fig. 10c, with the principal octahedral planes in the diagonal positions shown, 40° and 30° to the vertical, and the other two sets of octahedral planes nearly horizontal.

Some of these experiments were performed with all surfaces of the specimen outside of the jaws free and others with brass blocks just a little narrower than the specimen clamped firmly against it on both sides by means of side plates screwed to the jaws at A in Fig. 12, and a corresponding position on the underside.

Specimens were reduced in thickness from 5 to 30 per cent. in this manner, both with and without sidewise restraint, and in no case were visible twin lamellae formed.

The X-ray pattern of a specimen reduced 5 per cent. with free surfaces is shown in Fig. 16 and the corresponding gnomonic chart in Fig. 17. The beam was directed at right angles to the dodecahedral surface through a

FIG. 17.—GNOMONIC PROJECTION OF REFLECTING PLANES SHOWN IN FIG. 16.

small slice of the specimen obtained by embedding it in Wood's metal, cutting in half and etching in nitric acid to the desired thickness of about 0.010 inch.

Some asterism is evident in the diffraction spots but the distortion is not sufficient to obliterate the ordinary symmetry characteristics of projections in the dodecahedral plane. Furthermore, there are no spots in the pattern of Fig. 16 which from their position could have come from planes in a possible twin crystal and would require indices from this source in order to permit reflection according to the fundamental law,

$n\lambda = 2d \sin \theta$, within the range of wave lengths available ($n\lambda$ min = approx. 0.27Å).[15]
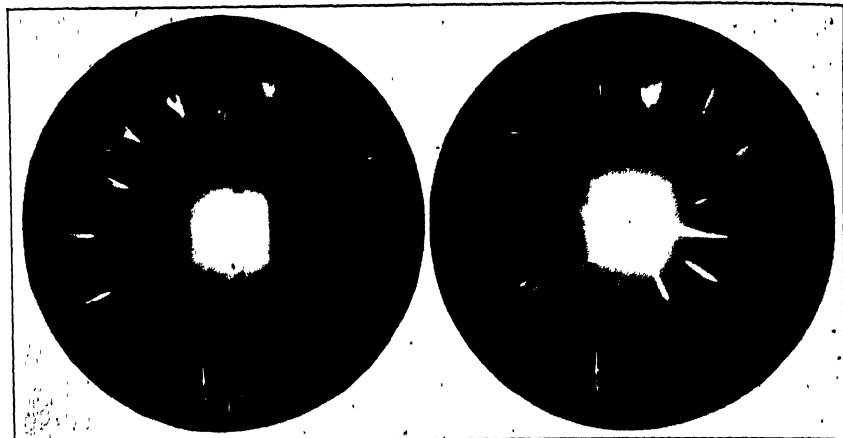

FIG. 18.—DIFFRACTION PATTERN OF A CRYSTAL REDUCED 20 PER CENT. IN THICKNESS.

FIG. 19.—DIFFRACTION PATTERN OF CRYSTAL REDUCED 30 PER CENT. IN THICKNESS.

The X-ray pattern of a specimen reduced 20 per cent. in thickness, shown in Fig. 18, revealed an irregular spreading and lengthening of the spots previously seen, which doubtless corresponds to slip along {111} planes and some form of rotation about an axis lying either in the slip plane or normal to it. The exact nature of this distortion cannot be determined from the pattern but it is especially noteworthy that the specimen itself did not recrystallize or form twin bands on annealing at 600° C. The pattern after annealing is substantially unchanged.

When the specimen that gave the pattern of Fig. 18 was deformed an additional amount, making the total correspond to a 30 per cent. reduction in thickness, it gave the highly asterized pattern shown in Fig. 19 and, although showing no visible deformational twin
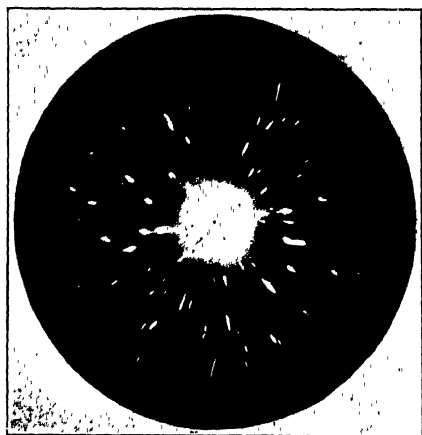
FIG. 20.—DIFFRACTION PATTERN OF CRYSTAL REDUCED 30 PER CENT. IN THICKNESS AND ANNEALED.

[15] In order to survey this situation thoroughly projections were made of the principal planes of possible twin crystals in the original dodecahedral plane and formulas for transferring indices from these to planes of the original crystal were applied.

lamellae, recrystallized on annealing with the usual formation of twin bands. After recrystallization, the pattern, shown in Fig. 20, no longer represents reflections from the planes of a single crystal.

Deformation by Rolling

Previous observations on zinc[16] have shown that single-crystal sections may be converted entirely into twin crystals by rolling on their basal planes in the direction of a normal to a first order prismatic plane. The twins form on conjugate planes of form $\{10\bar{1}2\}$ parallel to the axis of a roll and equally inclined, at an angle of 47°, to the horizontal.

Norton and Warren,[17] discussing the stresses encountered in rolling, show that the metal between the rolls is in a state of longitudinal tension with superimposed compression giving rise to maximum shearing stress along planes inclined less than 45° to the horizontal. It is stated that "slip will take place in any crystals having (slip) planes in such an orientation with a resulting rotation of these planes toward the direction of rolling."

In the experiments with zinc, shear on these planes resulted quantitatively in twinning before any considerable reduction in thickness occurred, and therefore before any marked rotation of the planes could ensue.

A similar geometrical arrangement would be instituted in the case of a copper crystal by rolling on cubic planes in the direction of a normal to a dodecahedral plane, except that the reduction necessary for quantitative twinning on the octahedral planes (inclined about 55° to the horizontal) would be some 29.3 per cent. instead of 6.75 per cent. in the case of zinc.

Experiments of this sort were performed without any evidence of twin lamellae or other deformational bands after careful polishing and etching. The prepared surface (001) looked like the uniformly reflecting surface of an undeformed crystal. This material gave a highly asterized X-ray pattern and recrystallized with twinning on annealing. The pattern after annealing was similar to that shown in Fig. 20.

Deformation by Impact

Mathewson and Edmunds[18] produced Neumann bands in ferrite by securely clamping a thin crystal between strips of brass and hammering the assembly edgewise. These conditions were reproduced in several experiments with copper crystals cut into thin sections bounded by cubic

[16] K. R. Van Horn: Effect of Stress on Zinc Single Crystals. M. S. Report, Yale University, 1928.

[17] J. T. Norton and B. E. Warren: Plastic Deformation of Metals. Proc. Inst. Met. Div., A. I. M. E. (1927) 361.

[18] C. H. Mathewson and G. H. Edmunds: Op. cit.

planes.   Previously polished sections showed characteristic slip planes, intersecting at approximately 90° after the deformation but twin bands could not be detected.   As in the case of the rolled specimens, X-ray patterns were highly asterized and recrystallization with abundant evidence of twinning occurred on annealing.

CONCLUSION

As a brief and general conclusion, it may be stated that every attempt to cause the slip on octahedral planes in a copper crystal to take the twinning direction [112] instead of the preferred direction [110] was unsuccessful, so that twinning by pure shear according to the simple diagram given in Fig. 3 appears to be out of the question in this material.

As to the origin of twin crystals visible after annealing, it may be argued that they occur only after deformation of a complex nature in which slip on one set of octahedral planes is modified by simultaneous slip involving atoms in the same field of attraction, on a crosswise set of octahedral planes.   Thus, certain [110] rows of atoms originally guided in their slip by adjacent rows must behave differently when these adjacent rows move out of position by slip in another plane.

It is believed that some complication of this sort is responsible for the first appearance of twin bands, as in Fig. 2, in the form of nuclei, which grow into larger bands or become absorbed by other crystals during the course of annealing.

DISCUSSION

O. W. ELLIS, Toronto, Ont.—An interesting thing is the fact referred to on page 80, that "the X-ray pattern of a specimen reduced 20 per cent. in thickness, shown in Fig. 18, revealed an irregular spreading and lengthening of the spots previously seen." The authors continue, "The exact nature of this distortion cannot be determined from the pattern but it is especially noteworthy that the specimen itself did not recrystallize or form twin bands on annealing at 600° C."   This is in line, of course, with some of the discoveries that were made by Miss Elam in her experiments on aluminum crystals.

What I should like to ask Dr. Mathewson is this: Did he make any determinations of the amount of rolling which could be given without recrystallization recurring? Further, did he determine in any of the experiments what change in orientation within the single crystal occurred as the result of deformation and subsequent annealing, if any at all?

L. W. McKEEHAN, New Haven, Conn.—I want to emphasize and amend a statement in the original paper (p. 63): "This is the form of movement naturally taken by balls piled on one another in the close-packed {111} arrangement, when tilted

and allowed to roll under the influence of gravity. This is probably a fact of only passing significance, as it does not take into account the forces between atoms in various directions."

When the structures of metal crystals were worked out by X-rays, it was interesting and at once pounced upon that the simpler structures, like that of copper, were close-packed in the sense that an assembly of spheres could take such structures in arrangements of least total volumes. A good deal of the early discussion was colored by this view. The extreme expression was made perhaps by a couple of Englishmen, Millington and Thompson, who dealt with the deformation of ping-pong ball piles and tried to explain the actual deformation taking place in metal crystals on that basis.

This paper shows more clearly than any previous paper that this naïve point of view cannot be held. If copper atoms are balls piled on one another, they certainly do not behave so when we attempt to force them to slip, because the direction of motion required for twinning is just the way it would be easiest, and the direction of slip that actually occurs is the hardest way to move a plane of close-packed balls over an adjacent plane. Of course the answer, as suggested by the authors, is that the atoms are not effectively spheres. They have preferences and objections toward their neighbors arranged in much less than spherical symmetry.

C. H. MATHEWSON.—The answer to both Dr. Ellis' questions is no. We did not devote nearly as much attention to the rolling experiments as we did to the experiments on stressing crystals in the special vise. But I feel confident that the amount of reduction that is necessary in rolling a single crystal to produce later recrystallization is rather small. There is almost immediately a crumbling effect and on annealing recrystallization readily occurs.

We did not determine change of orientation in these experiments. From the very nature of the experiments we expected to retain the original orientation and also to obtain the twin configuration in parts of the crystal. So we did not consider it desirable to utilize severe reductions.

Dr. McKeehan's remarks require little or no comment on my part. The point that he emphasizes struck me also as very interesting. It is certainly true that in a simple model made of spheres the easiest movement occurs in the twinning direction. However, in the copper crystal the elements cannot be made to move in this direction.

Thermal Conductivity of Copper Alloys, I.—Copper-zinc Alloys

By Cyril Stanley Smith,* Waterbury, Conn

ALTHOUGH not of the same importance as electrical conductivity, the capacity for conducting heat is nevertheless a very important property of metals and alloys. A knowledge of thermal conductivity is of value in selecting alloys for many purposes and in the calculation of the efficiency of apparatus which is being designed. Unfortunately, the determination of thermal conductivity is extremely slow and tedious, consequently few data have been obtained. A further reason for the lack of information is that there has long been an impression that the thermal conductivity of an alloy is directly proportional to the electrical conductivity and that it can therefore be calculated from the latter. The Wiedmann-Franz-Lorenz law of constant ratio of the two conductivities holds with a considerable degree of precision for all the pure metals, but appreciable deviations occur in certain alloys—particularly those containing nickel—and it seems difficult to predict exactly what the ratio will be. Therefore direct determinations of thermal conductivity should be made whenever the results are needed with any accuracy.

This research is intended eventually to cover all the alloys of copper that are of commercial importance, including the binary alloys of copper with zinc, tin, aluminum, nickel, silicon, manganese, cadmium and phosphorus, and the ternary alloys copper-nickel-zinc, copper-nickel-silicon, copper-manganese-silicon, copper-zinc-tin, etc. Most of these alloys are customarily used in the wrought condition and therefore were tested in the form of annealed rods. A limited number of sand castings were also obtained and examined.

This paper contains a complete review of all the previous work that has been done on copper alloys, and includes a detailed description of the apparatus and method of procedure used in the present research, together with the new results obtained on the copper-zinc series, which is the only one completed at the present time. Subsequent papers describing the other alloys will contain the experimental results and discussion only.

Previous Work

Copper

The conductivity of copper has been studied by many observers since the pioneer work of Wiedemann in 1859. The majority of these measure-

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*Research Laboratory, The American Brass Co.

ments were made with such crude apparatus and such impure material that the results are absolutely worthless, but for the sake of completeness they are included in Table 1, which gives, in chronological order, the more important determinations which the author has been able to find in a fairly exhaustive search of the literature.

TABLE 1.—*Thermal Conductivity of Copper*

Year	Investigator	Reference Number[a]	Thermal Conductivity at 20° C. Cal./Sq. Cm./Cm./Sec./° C.	Electrical Conductivity at 20° C. Per Cent. I. A. C. S.
1859	Wiedemann	35	0.736	84.0
1861	Ångstrom (1)	2	0.999 (0° C.)	
1861	Ångstrom (2)	2	0.865 (0° C.)	
1872	Weber	34	0.98	
1872	Neumann	26	0.665	77.4
1888	Berget	6	1.040	
1895	Gray	13	0.960	99.5
1895	Child, Quick and Lamphear	7, 28	0.979	
1900	Jaeger and Dieselhorst	19[b]	0.917	97.8
1900	Gruneisen	16[b]	0.934	98.2
1902	Schaufelberger	29	0.943	
1905	Glage	12	1.120 (75° C.)	
1908	Lees	23[b]	0.916	97.4
1910	Hering	18	1.5	
1915	King	20	0.912	
1915	Meissner (1)	25[b]	0.933	102.2
1915	Meissner (2)	25[b]	0.916	99.9
1916	Schott	31	0.936	100.0
1918	King	20	0.920	
1919	Sedstrom	32	0.782	52.0
1919	Pfleiderer	27	0.913	96.7
1923	Williams and Bihlman	37	0.90 (150° C.)	
1925	Schofield	14[b]	0.910	99.6
1926	Angell	1	0.921	
1928	Ellis, Morgan and Sager	10	0.919	100.1

[a] The numbers refer to the list given on page 104.
[b] Important references.

Several important references dealing solely with the conductivity at low temperatures have been omitted. Many of the earlier workers expressed their results as a percentage of the conductivity of pure silver. Since even at that time silver was obtainable comparatively pure, the present accepted value for the thermal conductivity of silver (1.00 cal./sq. cm./cm./sec./° C.) has been taken in converting these results to cal./sq. cm./cm./sec./° C. units. Appropriate corrections have been applied to the results, wherever they warrant it, to reduce the values to

20° C. The electrical conductivity of the copper used has also been given, when known, as an indication of its purity.

Of these figures, the ones that seem most reliable are those of Jaeger and Dieselhorst, Gruneisen, Lees, Meissner, and Schofield. They all seem to have performed careful work, and the agreement of their results is fairly good. A weighted average of all the results published since 1900 is 0.9207 cal./sq. cm./cm./sec./° C., and the corresponding average electrical conductivity 99.3 per cent. International Annealed Copper Standard. It is probable that pure copper, which has an electrical conductivity of about 102.5 per cent., would have a thermal conductivity proportionately higher.

Copper-zinc Alloys

Although of considerable industrial importance, the copper-zinc series has received comparatively little attention, and the published data on thermal conductivity are conflicting and probably unreliable. Table 2 gives in detail all the values that have been published, reduced to 20° C. where possible and arranged in order of increasing zinc content.

TABLE 2.—*Thermal Conductivity of Copper-zinc Alloys*

Investigator, Reference Number	Zinc, Per Cent. by Weight	Thermal Conductivity at 20° C. Cal./Sq. Cm./Cm./Sec./° C.
17	3.11	0.652
17	5.00	0.512
32	7.3	0.442
35	11.0	0.273
35	13.0	0.299
32	14.3	0.328
35	18.0	0.311
11	18.0 Small grain size	0.304 (0° C.)
11	18.0 Large grain size	0.309 (0° C.)
32	27.9	0.280
9	28.71 + 1.0% Sn + Pb + Fe	0.224
23	30.0	0.260
35	32.0	0.258
32	33.1	0.265
14	38.5 + 0.30% Mn	0.188
24	"Red brass"	0.253
24	"Yellow brass"	0.213
6	"Brass"	0.262
26	"Brass"	0.181
12	"Brass"	0.375 (75° C.)

Copper-nickel and Copper-nickel-zinc Alloys

Several isolated alloys of copper with nickel and with nickel and zinc have been examined, and the complete binary series copper-nickel has

been studied by both Sedstrom[32]* and Smith.[33]   Table 3 gives all the information available, again reduced to 20° C.

TABLE 3.—*Copper-nickel and Copper-nickel-zinc Alloys*

Investigator, Reference Number	Composition, Per Cent. by Weight			Thermal Conductivity at 20° C. Cal./Sq. Cm./Cm./Sec./° C.
	Copper	Nickel	Zinc	
32	95.1	4.9		0.215
	90.0	10.0		0.136
	79.9	20.1		0.079
	60.0	40.0		0.050
	39.1	60.9		0.055
	18.4	81.6		0.062
	0.0	100.0		0.141
33	90.0	10.0		0.093 (57° C.)
	70.0	30.0		0.058 (57° C.)
	60.0	40.0		0.054 (57° C.)
	50.0	50.0		0.054 (57° C.)
	40.0	60.0		0.054 (57° C.)
	30.0	70.0		0.069 (57° C.)
	20.0	80.0		0.073 (57° C.)
	0.0	100.0		0.140 (57° C.)
17	94.1	3.9		0.208
	88.7	17.3		0.081
19	60.0	40.0		0.054
10	55.0	45.0		0.055
16	54.0	46.0		0.048
10	28.0	70.0	2.0% Fe	0.083
3	"Constantan"			0.067
23	63.0	15.0	22.0	0.059
	63.0	15.0	22.0	0.060
24	"Neusilber"			0.074
26	"Neusilber"			0.066

It should be mentioned that the ratio of thermal to electrical conductivity is much higher for alloys containing nickel than for the pure metals or the brasses and bronzes.

Copper-tin and Copper-aluminum Alloys

Table 4 summarizes the results obtained by various investigators on copper-tin alloys, many of them containing phosphorus, and on the aluminum bronzes.

* Numbers in parentheses refer to list of references at end of paper.

TABLE 4.—*The Tin and Aluminum Bronzes*

Investigator, Reference Number	Composition, Per Cent. by Weight				Thermal Conductivity Cal./Sq. Cm./Cm./Sec./° C.
	Cu	Sn	P	Al	
17	95.0	5.0			0.176 (20° C.)
15	90.1	9.9			0.105 (13° C.)
	75.5	24.5			0.059
	24.9	75.1			0.139
	9.7	90.3			0.131
	0.0	100.0			0.142
14	91.7	8.0	0.30		0.108
	87.2	12.4	0.40		0.087
	90.0	10.0	Small amt.		0.100
9	87.8	11.3	0.35		0.128
37	89.9	0.47		9.04	0.174 (220° C.)
3	90.0			10.0	0.180
14	90.0			10.0	0.122
33	90.0			10.0	0.195 (52° C.)
	80.0			20.0	0.070 (52° C.)
	70.0			30.0	0.178 (52° C.)
	60.0			40.0	0.180 (52° C.)
	50.0			50.0	0.283 (52° C.)

Miscellaneous Alloys

There is a quantity of information in the literature on various complex or special copper alloys, some commercial and others made for experimental purposes. In Table 5 all these miscellaneous alloys are listed.

Tables 2 to 5 contain a complete list of the thermal conductivities of all the copper alloys that have been reported on in the literature. This is a remarkably small number considering the vast number of alloys and the real need for accurate information, and it can readily be seen that there is plenty of scope for further work, particularly as many of the results published are obviously inaccurate.

METHODS OF DETERMINATION

All methods for the determination of thermal conductivity are based on the measurement of the flow of heat produced in a rod of known dimensions by a known temperature gradient. If a bar of uniform cross-section is heated at one end and cooled at the other, and if precautions are taken to prevent lateral loss of heat, the amount of heat put in at the hot end will be exactly equal to that removed at the cold end and can be measured at either point. Probably the most accurate method is to determine the heat input by using an electric resistance coil and measuring the power consumed. However, to ensure that all the heat from the

TABLE 5.—*Miscellaneous Copper Alloys*

Investigator, Reference Number	Composition, Per Cent. by Weight										Thermal Conductivity at 20° C. Cal./Sq. Cm./Cm./Sec./° C.
	Cu	Zn	Sn	Ag	Pb	Ni	Mn	P	As	Fe	
33	90					10					0.065 (59° C.)
	80					20					0.041 (59° C.)
	70					30					0.032 (59° C.)
	60					40					0.031 (59° C.)
	40					60					0.027 (59° C.)
	95			5							0.777 (62° C.)
	90			10							0.723 (62° C.)
	80			20							0.639 (62° C.)
	70			30							0.628 (62° C.)
	60			40							0.658 (62° C.)
	55			45							0.751 (62° C.)
	50			50							0.747 (62° C.)
	45			55							0.749 (62° C.)
27	99.4						0.63				0.250 (30° C.)
	98.0						1.98				0.125 (30° C.)
16	Bal.								Trace		0.340
	Bal.								Large amt.		0.0995
37	99.4					0.20			0.23		0.50 (125° C.)
9	99.5					0.02			0.39		0.508
19	85.7	7.2	6.4			0.6					0.143
9	87.2	2.2	10.0		0.35					0.21	0.131
14	88.0	2.0	10.0								0.118
	87.8	2.0	10.0					0.15			0.102
	92.8	2.0	5.0					0.15			0.189
9	85.0	5.0	8.7	Al	0.98					0.21	0.168
	57.14	37.5	0.26	0.95			2.33			1.8	0.164
23	84					4.0	12				0.053
19	84					4.0	12				0.052

coil is transferred to the specimen, the coil must be completely embedded, thus requiring the specimen to be intricately machined. A simpler method, although less accurate, is to measure the heat extracted from the cold end by means of a stream of water, the temperature of which is measured both before and after its contact with the bar. This method, of course, is limited to comparatively low temperatures, since the cold end of the bar must be almost at room temperature.

Another method, which has been used to some extent, consists in clamping both ends of the bar in water-cooled clamps and passing a heavy current through it. From measurements of current and potential and of the maximum temperature reached in the center of the bar, the thermal and electrical conductivity can be obtained simultaneously.

Forbes' method, which was used to some extent by the earlier workers, consists of determining the temperature gradient in a long bar which is heated at one end and exposed to free air for most of its length. The temperature gradient, combined with a knowledge of the amount of heat radiated per unit length, which is obtained by an independent cooling curve of the entire bar, enables the conductivity to be calculated.

The velocity of propagation of a symmetrical wave of heat along a wire can be used to calculate the thermal conductivity. This method has the great advantage that small samples in the form of wire can be used, but this is outweighed by the fact that the density and specific heat of the alloy at the temperature of the determination must be known.

Several workers have designed apparatus in which a little accuracy has been sacrificed in order to use a simple form of sample and to have an apparatus that could be manipulated easily and thus be suitable for measurements in an industrial laboratory. Of these, the apparatus of Wilkes,[36] Donaldson,[9] Williams and Bihlman,[37] and Griffiths[14] particularly should be mentioned. In all these the heat flow is measured by a water-flow calorimeter on the cold end of the bar, the other end being heated by a resistance coil. In order to cut down heat loss from the surface of the specimen, the guard-ring principle is usually used. A tube surrounds the specimen and is maintained with the same temperature gradient, the space between the two being packed with some loose insulating material. The guard ring may either be heated independently of the specimen by a separate heating coil or it may be screwed on to a heavy copper block which also holds the specimen, thus ensuring that both are at the same temperature. In Griffiths' apparatus the guard ring is dispensed with and the bar covered with a layer of insulating material of known properties, permitting the losses to be calculated and appropriate corrections made to the results.

APPARATUS

The apparatus constructed for the present research was essentially similar to that of Wilkes, although several minor improvements were made in order to give more accurate results. It is shown in Fig. 1. The specimen and guard-ring tube were both attached to a heavy electrically heated copper block. The water for cooling the guard ring flowed through a groove machined on the outside, covered with a copper sheet soldered in position.

The specimens were 13.25 in. over-all length, with a 10 in. test length, 0.750 in. dia. One end was threaded for a distance of 1 in. with a standard $\frac{3}{4}$-in. thread (10 threads per inch) to fit the heater block, and the other end had a fine thread (24 per inch) for a length of $2\frac{1}{4}$ in. to screw into the cooling head. A slot cut in the end of the rod served the double purpose of providing a passage for the cooling water and to take a key for unscrewing the bar.

The cooling head had, superimposed on the fine thread, a spiral groove of $\frac{1}{2}$ in. pitch through which water flowed directly in contact with the bar. The difference in temperature between incoming and outgoing water was measured by a six-element differential thermocouple, the junctions fitting in two wells which were arranged to lie alongside the
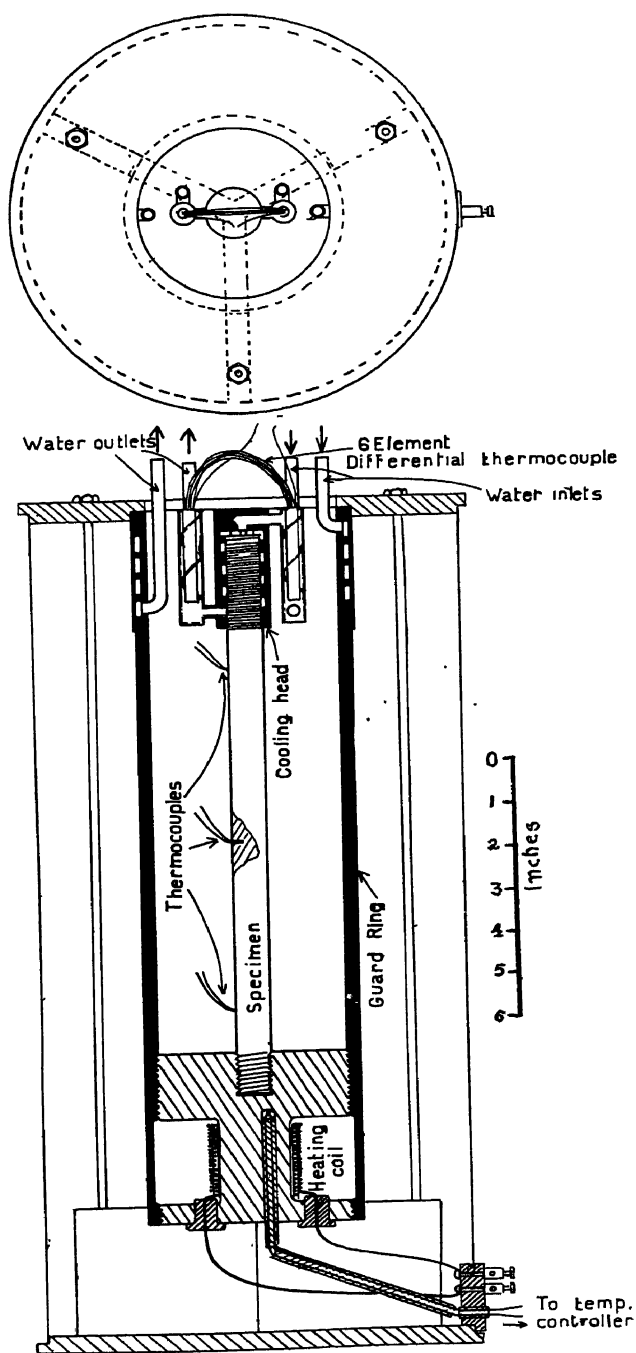
FIG. 1.—APPARATUS FOR DETERMINATION OF THERMAL CONDUCTIVITY.

cooling head, inside the water-cooled section of the guard ring, and were therefore protected from changes in atmospheric temperature. This arrangement required the guard ring to be of larger diameter than that usually employed. This was an advantage, because it permitted a greater thickness of insulating material between the specimen and the guard ring and therefore reduced the magnitude of the effect of any difference in temperature between the two.

The guard ring with the heater block inserted was permanently installed in an outer casing of galvanized iron, 9 in. dia., packed with "Sil-o-cel" powder (diatomaceous earth).

The differential thermocouple was built of 0.005-in. copper and 0.014-in. constantan wires, with soft-soldered junctions. The junctions were insulated from each other by paper strip, and the whole impregnated with paraffin wax to improve the conductivity. Very fine wire had to be used in the construction of the couple, because the conduction of heat became appreciable when wire of larger size was used.

The temperature gradient in the specimen was measured by three thermocouples, the outer ones being 8 in. apart. The couples were made of 0.020-in. copper and 0.025-in. constantan wires, and the junctions were made by pegging the bare ends of the wires, with brass pegs, into holes of 0.060 in. dia. drilled in the specimen. The wires were insulated from each other and supported inside the apparatus by twin-bore alundum tubing. The ends of the constantan wires were soldered to copper extensions and the junctions kept in a vacuum bottle filled with ice. The e.m.f. was measured with a Leeds and Northrup type K potentiometer, reading to 0.001 millivolts.

. Thermocouples were inserted in the guard ring at points exactly opposite the thermocouples in the specimen, and it was found with the first apparatus that the hot end was about 10° C. cooler than the specimen at the same point. An auxiliary winding of five turns was therefore wrapped round the end of the guard ring, insulated with sheet mica and connected in series with the main heating coil. This was just sufficient to equalize the temperatures of the guard ring and specimen; the difference was never any more than 5° C. and usually less than 2° C.

The only source of current available for heating was a lighting circuit of variable voltage, and since it was necessary to hold the apparatus at a constant temperature for several hours before taking readings, it was practically essential to employ some form of temperature control to prevent undue fluctuation. A thermocouple installed permanently in the heater block was connected with a Leeds and Northrup recording controller which was adjusted to the finest possible range of control, and the relay was arranged to switch only a small portion of the total current necessary to heat the apparatus. The temperature did not vary by more than ±1° C. at the highest temperature used, and the control was even

closer than this at lower temperatures. However, even an error of this magnitude would affect the results more than was permissible, consequently average values were always taken for the temperatures over two complete control cycles.

The water for cooling was obtained from a constant-level overflow tank, which was of such capacity that the water had time to reach an approximately steady temperature before it was used. The rate of flow of the cooling water was measured by determining with a stop-watch the time taken to fill a measuring flask of 1000 or 500 c.c. capacity.

The procedure in obtaining a set of readings was as follows: The water flow rate was adjusted, and the heater block heated to the desired temperature and held there under control for at least 3 hr. Readings were then taken of all three thermocouples on the specimen at times that would give both the maximum and the minimum temperatures produced by the control cycle. The measuring flask was then placed under the water nozzle and the watch was started. A reading of the e.m.f. of the differential thermocouple was taken every 30 sec. during the measurement of the flow. Two or more series of measurements were always made in order to bring the total time to at least 10 min., hence about 20 readings of temperature difference were obtained and averaged. To ascertain

TABLE 6.—*Typical Example of Calculation of Thermal Conductivity*

Bar No. 14, 9.91 per cent. Zn. Diameter, 1.904 cm. Area, 2.8472 sq. cm.
Distance between thermocouples, a and b = 10.16 cm., b and c = 10.16 cm.

$$\text{Couple } a = 10.625 \text{ mv.} = 284.1° \text{ C.}$$
$$\text{Couple } b = 6.470 \text{ mv.} = 185.4° \text{ C.}$$
$$\text{Couple } c = 2.512 \text{ mv.} = 79.0° \text{ C.}$$

Differential thermocouple = 0.4271 mv. = 2.315° C.
Water flow of 1000 c.c. in 150.5 seconds.

$$\text{Heat flow} = \frac{1000 \times 2.315}{150.5} = 15.38 \text{ cal. per sec.}$$

Temperature difference, $a - b$ = 98.7° C.

$$\therefore \text{ Thermal conductivity} = \frac{15.38 \times 10.16}{98.7 \times 2.847} = 0.5561 \text{ cal./sq. cm./cm./sec./° C.}$$

at an average temperature, $\dfrac{a + b}{2} = 234.8°$ C.

Temperature difference, $b - c$ = 106.4° C.

$$\therefore \text{ Thermal conductivity} = \frac{15.38 \times 10.16}{106.4 \times 2.847} = 0.5160 \text{ cal./sq. cm./cm./sec./° C. at an}$$

average temperature of 132.2° C.

Temperature difference, $a - c$ = 205.1° C.

$$\therefore \text{ Thermal conductivity} = \frac{15.38 \times 20.32}{205.1 \times 2.847} = 0.5345 \text{ cal./sq. cm./cm./sec./° C. at an}$$

average temperature of 181.6° C.

whether the temperature gradient had changed during the experiment, the high and low readings of the three thermocouples were again determined. The rate of water flow was then changed and the apparatus left for a further 2 or 3 hr. at the same temperature to reach equilibrium, after which a second set of readings was taken. The temperature was then changed and the whole procedure repeated.

In this way four distinct sets of readings were obtained, and since each set of readings gave values for the conductivity at three different temperatures, 12 points on the temperature-conductivity curve were obtained. It was soon found that within the limits of experimental error, this curve was a straight line. From this curve the conductivities at both 20° and 200° C. were read. The method of calculation used will be obvious from the typical example given in Table 6.

Accuracy of Measurements

The accuracy of the results depends primarily on the accuracy of the temperature measurements along the bar and the temperature difference between the water entering and leaving the cooling head. The copper-constantan thermocouples used for measuring the temperature at the three points on the specimen were calibrated with extreme care at the sodium sulfate transition point (32.38° C.), the boiling point of water (100° C. at 760 mm. pressure), and the freezing points of tin (231.85° C.) and lead (327.4° C). Using these four calibration points the constants in the equation $e = at + bt^2 + ct^3$ were derived and the complete curve plotted. The thermocouples were recalibrated when the work was half completed and found to be within 0.2° C. of the original calibration curve at all temperatures.

The differential thermocouple was standarized against two mercury-in-glass thermometers reading to 0.01° C. which had recently been certified by the U. S. Bureau of Standards. The calibration of this thermocouple is probably the least accurate part of the whole determination, but it is certain that the error is less than 1 per cent., since the calibration curve was determined for temperature differences of about 2°, 5° and 10° C., and extrapolated at lower temperatures.

Any difference in temperature between the specimen under test and the guard ring will result in a flow of heat away from or to the specimen. The amount of this will depend on the thickness and thermal conductivity of the insulating material, and on the temperature difference between the bar and the guard ring. Although both ends of the guard ring were maintained at the same temperature as the ends of the specimen, a different temperature coefficient would result in a different temperature gradient in the center. On calculating the distribution curves for copper and 70/30 brass, of which the guard ring was made, it was found that

there was a difference in temperature of about 5° C. at the center, the ends being at the same temperature. However, there was a thick layer of Sil-o-cel between the guard ring and the bar, and the loss or gain was therefore quite negligible.

The heat flow due to a difference in temperature between the guard ring and bar is given by the following formula.

$$H = \frac{2\pi\, kL(t_1 - t_2)}{\log_e \dfrac{(r_2)}{(r_1)}}$$

where k is the thermal conductivity of Sil-o-cel (0.0015 cal./sq. cm./cm./- sec./° C.), t_1 and t_2 and r_1 and r_2 are the temperatures and radii of the bar and guard ring respectively, and L is the length under consideration. Assuming a temperature difference of 10° C. over the whole length of the bar, the heat flow would be 0.114 calories per second, but since the difference is much less than 10° C., and never exists over the whole length of the bar, it can be seen that the error due to this cause is very small.

Another possible source of error lies in the conduction of heat along the thermocouples and thermocouple sheaths. This was calculated and found to be equal to 0.037 cal. per sec., assuming perfect thermal contact of the thermocouple sheaths with the bar, and taking the conductivity of the alundum as 0.0083 cal./sq. cm./cm./sec./° C. However, in the actual experimental set-up only the thermocouple wires were in contact with the specimen, and the sheaths, which account for the greater part of the conductivity, were always much closer to the guard ring than to the bar. Furthermore, the wires left the specimen almost at right angles, in a direction in which there would be no heat flow on account of the guard ring. It is obvious, therefore, that there could be no appreciable error caused by the thermocouples or their sheaths.

There seem to be certain difficulties inherent in the water-flow calorimeter. Even with a constant flow of water the temperature seems to fluctuate to a slight extent, but the main trouble is due to changes in the rate of flow—presumably due to the formation and movement of bubbles of air. The trouble was largely eliminated by measuring both the flow and temperature difference over a long period of time, and averaging the figures, which then checked quite closely even when the flow rate varied.

Taking into account all possible sources of error, it is thought that the maximum error in the results of the present work is about 2 per cent., and most of the results are probably more accurate than this.

ELECTRICAL CONDUCTIVITY MEASUREMENTS

Although it would be a great advantage to determine the electrical conductivity at a series of temperatures in order to compare its variation

with the variation of thermal conductivity, it was not found convenient to do this at the present stage of the work, and the electrical measurements were limited to the determination of the resistivity and conductivity at 20° C. These measurements were made by Charles F. Schmid at the Ansonia Laboratory of The American Brass Co., and the writer wishes to express his gratitude to Mr. Schmid for the prompt and accurate way in which he and his staff handled these determinations. The determinations were of a routine nature but the results are nevertheless believed to be more accurate than the thermal conductivity measurements.

TABLE 7.—*Composition and Heat Treatment of the Copper-zinc Alloys Used*

Bar No.	Composition, Per Cent. by Weight				Annealing Treatment[a]		Dia. Avg. Grain, Mm.	Structure
2	Cu 99.986	O 0.022	Fe 0.0016	S 0.0015	°C. 550	Hr. 1	0.075	
	Cu	Zn	Fe	Pb				
90	99.64	0.35	0.02	0.01	650	1	0.070	
89	99.45	0.51	0.01	0.01	650	1	0.110	
73	98.93	0.95	0.02	0.00	700	1	0.120	
12	96.94	3.04	0.02	0.00	700	¾	0.100	
13	95.21	4.77	0.02	0.00	700	¾	0.085	Homogeneous α
14	90.07	9.91	0.01	0.01	700	¾	0.095	
15	83.20	16.76	0.03	0.01	700	¾	0.125	
16	79.62	20.35	0.01	0.02	700	¾	0.190	
18	69.14	30.81	0.03	0.02	650	¾	0.075	
21	65.43	34.53	0.01	0.03	650	¾	0.080	
22	59.20	40.75	0.02	0.03	650	3	0.070	α + β
88	54.96	45.02	0.02	0.00	650	2	0.40	β
85	50.30	49.45	0.01	0.04	650	2	16.0	β + trace γ

[a] All bars air-cooled after annealing except bars 22, 88 and 85, which were cooled in furnace, 18 hr. to 450° C.

MATERIAL FOR INVESTIGATION

Most of the material for the investigation of the copper-zinc series was obtained from the mill, and represents normal high-grade commercial material. Four special alloys containing unusually high or low zinc were cast at the laboratory into billets 2¼ in. dia. and hot-rolled to ⅞ in. diameter.

Pieces were cut from each rod and annealed at a suitable temperature to cause recrystallization, but not high enough to cause abnormally

large grain growth.*   This was 700° C. in the case of most of the low–zinc alloys, and 650° C. for the high–zinc alloys.   The alloys containing beta (bars 22, 85, 88) were annealed for several hours at 650° C. and then cooled extremely slowly to 450° C. in order to ensure that they were in equilibrium as far as possible.   The annealing treatment which each bar received, together with the grain size produced, is given in Table 7. An analysis was made of every bar, and the results are included in Table 7.   The copper, lead and iron were determined on each sample, and the zinc was taken by difference except in the cases of the special alloys at each end of the series.

RESULTS OF INVESTIGATION

The value for the thermal conductivity of pure copper obtained by the author is 0.941 cal./sq. cm./cm./sec./° C. at 20° C.   This is the average
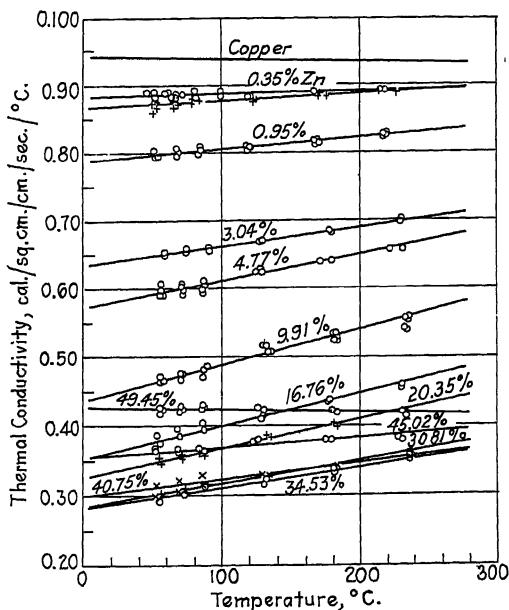
FIG. 2.—EFFECT OF TEMPERATURE ON THERMAL CONDUCTIVITY OF COPPER-ZINC ALLOYS.

of 16 independent determinations, and is thought to be accurate within ±0.005 cal./sq. cm./cm./sec./° C.   This is higher than the figures given by most other investigators, which average about 0.921 cal./sq. cm./-cm./sec./° C.   However, previous workers used copper of distinctly inferior electrical conductivity, averaging 99.3 per cent. I.A.C.S. while the copper used in the present work was extremely pure and had an

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* The alloy with 49.45 per cent. zinc (beta) did develop abnormal grain growth in places.   This is thought to be due to critical straining of the metal by the straightening before annealing.

electrical conductivity of 101.66 per cent., consequently it would be expected that the thermal conductivity would be proportionately high.

The results of the measurements on the copper-zinc series are given in Table 8 and shown graphically in Figs. 2, 3, 4 and 5.

TABLE 8.—*Thermal and Electrical Conductivity of Copper-zinc Alloys*

Bar No.	Per Cent. Zinc	Electrical Conductivity λ at 20° C., Ohm⁻¹ Cm. × 10⁴	Electrical Conductivity at 20° C., Per Cent. I.A.C.S.	Thermal Conductivity at 20° C., Per Cent. Copper	Thermal Conductivity K at 20° C., Cal./Sq Cm./Cm./Sec./° C.	Thermal Conductivity K at 200° C, Cal./Sq. Cm./Cm./Sec./° C.	Temperature Coefficient of Thermal Conductivity α at 20° C.	Wiedemann-Franz ratio $\frac{K}{\lambda T}$ × 10⁸ at 293° abs.
2	0.00	58.962	101.66	100.0	0.941	0.934	−0.000041	5.45
90	0.35	55.264	95.28	94.0	0.884	0.890	+0.000038	5.46
89	0.51	53.323	91.93	92.2	0.868	0.887	0.000121	5.56
73	0.95	47.685	82.21	84.2	0.792	0.822	0.000210	5.67
12	3.04	36.607	63.12	68.0	0.640	0.690	0.000434	5.97
13	4.77	33.062	57.00	63.4	0.579	0.650	0.000681	5.98
14	9.91	25 293	43.61	47.4	0.446	0 538	0.001021	6.02
15	16.76	20.108	34.67	39.1	0.361	0.445	0.001291	6.12
16	20.35	18.459	31.83	35.5	0.334	0.408	0.001231	6.18
18	30.81	15.857	27.34	30.8	0.290	0.349	0.001130	6.24
21	34.53	15.325	26.42	30.4	0.286	0.340	0.001049	6.37
22	40.75	16.700	28.79	32.2	0.303	0.345	0.000770	6.20
88	45.02	20.466	35.29	37.9	0 357	0.382	+0.000389	5.85
85	49.45	23.812	41.05	45.3	0.426	0 419	−0.000091	6.11

Fig. 2 shows temperature-conductivity curves for all the alloys. The decrease in conductivity as the amount of zinc in the alpha solid solution is increased is clearly shown, but the most striking thing about these curves is the fact that while the conductivity of copper *decreases* slowly as the temperature rises, that of the alpha solid solution alloys *increases* rapidly. Copper, therefore, has a small negative temperature coefficient and the alpha alloys have a large positive coefficient. The conductivity at any temperature, t, is given by

$$K_t = K_{20}[1 + \alpha(t - 20°)]$$

where K_{20} is the conductivity at 20° C., as given in column 6, Table 8, and α is the temperature coefficient, column 8, which is equal to the slope of the curve divided by the conductivity at 20° C.

Fig. 3 shows the thermal conductivity at both 20° and 200° C, the temperature coefficient at 20° C, and the Wiedemann-Franz-Lorenz ratio, $\frac{K}{\lambda T}$, where K is the thermal conductivity in cal./sq. cm./cm./-

sec./° C., λ the electrical conductivity in ohm^{-1} cm., and T the absolute temperature.   Fig. 4 gives on a larger scale the part of Fig. 3 up to 10 per cent. zinc, in order to show more clearly the changes which occur in that part of the diagram.
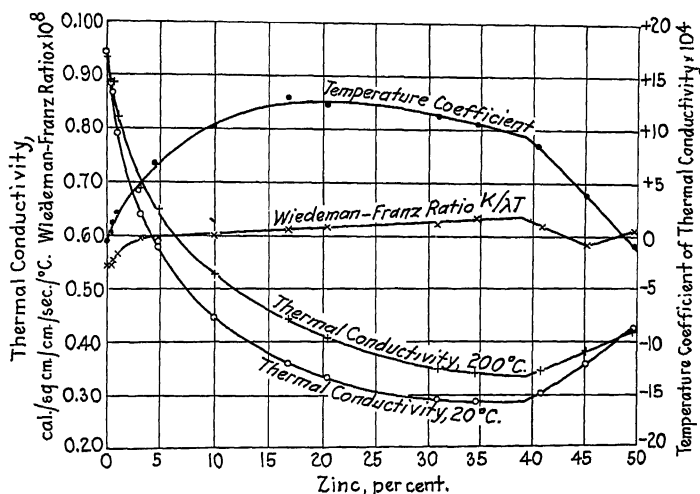

FIG. 3.—THERMAL CONDUCTIVITY OF COPPER-ZINC ALLOYS (0 TO 50 PER CENT. ZINC)
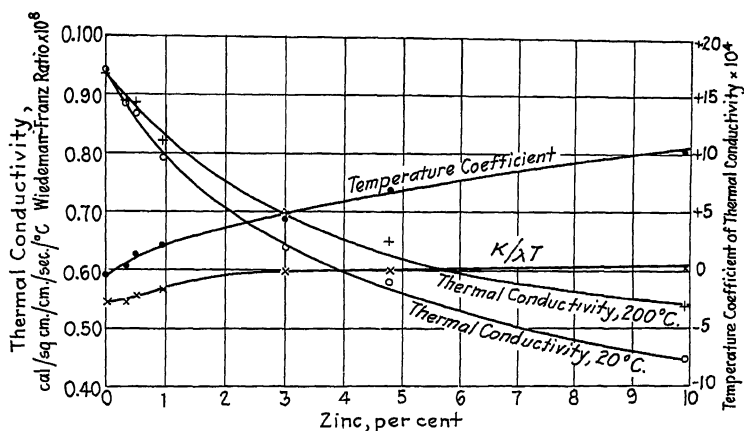

FIG. 4.—THERMAL CONDUCTIVITY OF COPPER-ZINC ALLOYS (0 TO 10 PER CENT. ZINC)

The rapid decrease in thermal conductivity as zinc is added to copper is to be expected.   The comparison of the two conductivities, Fig. 5, shows that the drop is not as rapid as the drop in electrical conductivity, and this is reflected by the figures for the Wiedemann-Franz-Lorenz ratio in Figs. 3 and 4.   The value of the ratio for pure copper is 5.45 × 10^{-9} ,while with 3 per cent. zinc it becomes 5.97 × 10^{-9}, and increases very slowly and linearly thereafter to the limit of the alpha range, 39

per cent. zinc, where it has the value 6.38 × 10⁻⁹. In Fig. 5, to permit easier comparison, the two conductivities are each expressed as a percentage of copper and plotted against composition. The electrical conductivity is expressed as a percentage of the International Annealed Copper Standard at 20° C, while the thermal conductivity is on the basis of Copper = 0.941 cal./sq. cm./cm./sec./° C. at 20° C. This makes the electrical conductivity scale slightly higher than that of the thermal conductivity, since pure copper is taken as 101.66 per cent. electrical and 100.00 per cent. thermal conductivity. Nevertheless, the electrical conductivity curve rapidly crosses the other and finally becomes practically parallel to it, about 4 per cent. below.
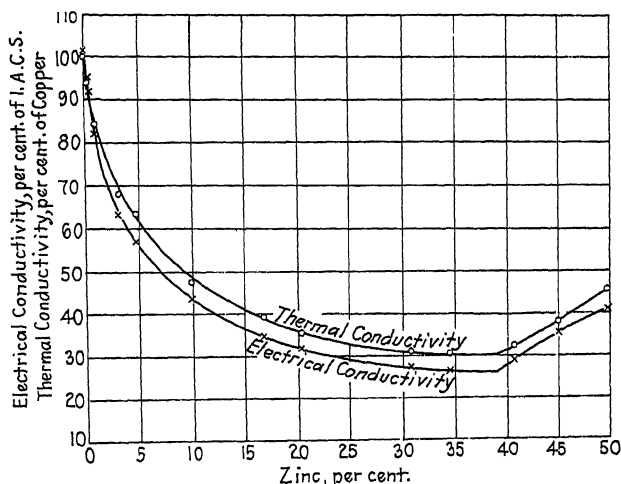
FIG. 5.—COMPARISON OF ELECTRICAL AND THERMAL CONDUCTIVITIES OF COPPER-ZINC ALLOYS (0 TO 50 PER CENT. ZINC) AT 20° C.

The reason for the less rapid decrease of thermal conductivity as the amount of zinc in the solid solution increases may perhaps be due to the fact that electrical conductivity depends entirely on free electrons, while thermal conductivity is composed of the sum of heat carried by free electrons and that carried by direct collision of atoms. Alloying has some effect on the free electrons and therefore affects the electrical conductivity greatly, but it will affect only that portion of the thermal conductivity that is dependent on electrons, and will be without effect on the portion that is due to the direct collision of atoms.

The appearance of beta in the alloys with more than 39 per cent. zinc causes a marked change in the direction of all the curves. The conductivity immediately begins to increase, while the temperature coefficient decreases rapidly and the Wiedemann-Franz-Lorenz ratio becomes appreciably less. It is interesting to note that copper-saturated

beta has a positive temperature coefficient while zinc-saturated beta has a negative temperature coefficient.

SPECIAL COPPER-ZINC ALLOYS

A number of special brasses, including Admiralty brass and some free turning leaded brasses, were also tested. Table 9 gives the complete analyses and the annealing treatment which the rods had received. In Table 10 are listed the thermal and electrical conductivities and temperature coefficient of these alloys. The negligible effect of lead, which can be seen on comparing bars 52 and 54 with bars 14 and 22 in Table 8, is to be expected, since lead is almost insoluble in copper-zinc alloys. Tin is soluble and reduces the conductivity appreciably. Bars 55, 56 and 57 show this, the reduction in conductivity being roughly proportional to the amount of tin. The binary copper-tin alloys will be described in the next paper.

TABLE 9.—*Composition and Heat Treatment of Special Brasses*

Bar No.	Composition, Per Cent. by Weight					Annealing Treatment[a]	
	Cu	Zn	Fe	Pb	Sn	°C.	Hr.
52	89.15	9.51	0 02	1 32		575	½
54	59.98	37.88	0.03	2.01	0.10	650	2
55	81.18	18.63	0.02	0.00	0.20	700	2
56	71.09	27.77	0.02	0.00	1.02	700	¾
57	59.85	39.36	0.02	0.07	0.70	650	3

[a] All bars air-cooled after annealing except bar 54, which was cooled in furnace 16 hr., to 450° C.

TABLE 10.—*Thermal and Electrical Conductivity of Special Brasses*

Bar No.	Electrical Conductivity, λ, at 20° C. Ohm^{-1} Cm. × 10^4	Electrical Conductivity at 20° C. Per Cent. I.A.C. S.	Thermal Conductivity at 20° C. Per Cent. of Copper	Thermal Conductivity, K, at 20° C. Cal./Sq. Cm./Cm./Sec./° C.	Thermal Conductivity, K, at 200° C. Cal./Sq. Cm./Cm./Sec./° C.	Temperature Coefficient of Therm. Cond, α, at 20° C.	Wiedemann-Franz Ratio, $\frac{K}{\lambda T}$ × 10^8 at 293° Abs.
52	24.541	42.31	45.9	0.432	0.511	0.001016	6.01
54	14.682	25.31	27.4	0.258	0.322	0.001384	5.99
55	18.674	32.20	36.3	0.341	0.409	0 001100	6.24
56	14.298	24.65	28 0	0.263	0.326	0.001330	6.29
57	15.146	26.11	29.6	0 279	0.320	0 000822	6.29

SUMMARY

This paper describes the first of a series of experiments to determine the thermal conductivities of all commercial alloys rich in copper. It contains a complete review of previous work, and gives in detail new data on the copper-zinc alloys up to 50 per cent. zinc. The thermal conductivity of the alloys decreases rapidly from 0.941 cal./sq. cm./cm./ sec./° C. for pure copper to 0.285 for the saturated alpha solid solution, 39 per cent. zinc. The appearance of the beta phase in the alloys causes an increase in conductivity and a very rapid decrease in the temperature coefficient. The decrease in thermal conductivity caused by adding zinc to copper is not as rapid as the decrease in electrical conductivity, although in general the two curves are similar in form.

APPENDIX A.—UNITS AND CONVERSION FACTORS

The results in the paper are expressed in the usual scientific units; *i. e.*, gram calories per second per square centimeter area per centimeter length per 1° C. temperature difference. This is written cal./ sq. cm./ cm./sec./° C., and is often called "calories per second per centimeter cube per degree centigrade."

The results were not sufficiently accurate to necessitate the specification of the calorie being used (*i. e.*, the 4°, 15°, 20° C, or mean calorie); indeed, no attempt was made either to control or measure the temperature of the water, which was usually about 15° C.

Figures in cal./sq. cm./cm./sec./° C. units can be converted to the ordinary engineering units by the following factors:

UNITS	FACTORS BY WHICH CAL./SQ. CM./CM./SEC./° C. SHOULD BE MULTIPLIED TO CONVERT TO DESIRED UNITS
Watt/sq. cm./cm./sec./° C	4.186
B.t.u./sq. ft./in./sec./° F	0.806378
B.t.u./sq. ft./in./hr./° F	2902.96
B.t.u./sq. ft./ft./hr./° F	241.91

These factors are calculated using the mean calorie [= 4.186 Joules (abs.)], and the mean British thermal unit [= 1054.8 Joules (abs.)] and taking 1 in. as equal to 2.5400 centimeters.

APPENDIX B.—INDIVIDUAL EXPERIMENTAL RESULTS ON EACH BAR

BAR, 90, 0.35 PER CENT. ZN		BAR 89, 0.51 PER CENT. ZN		BAR 73, 0.95 PER CENT. ZN		BAR 12, 3.04 PER CENT. ZN		BAR 13, 4.77 PER CENT. ZN	
° C.	K	° C.	K	° C	K	° C.	K	° C.	K
220.3	0 892	228	0.889	220	0.828	232 0	0 700	233 0	0.658
217 1	0 892	219	0 895	219	0 824	231.9	0.702	232.0	0.659
170 7	0.887	215	0 890	219	0 827	179 9	0.684	222 3	0.657
168 2	0 888	176	0 883	170	0 818	178.8	0 684	180.0	0.641
121.7	0 882	171	0.882	169	0 814	130.0	0 671	180.0	0.642
119.9	0.882	170	0 887	168	0 818	128 3	0.668	172 8	0.641
100 3	0 884	125	0 877	121	0 809	91 4	0.656	129 0	0 625
100.1	0 892	122	0 876	120	0.806	91.3	0 661	129 0	0.626
82 0	0 879	122	0 880	119	0.810	75.0	0.653	125.0	0.624
81 8	0.884	83	0 888	85	0 803	74 9	0.657	88 0	0.605
81 7	0 884	83	0.877	84	0.797	58 9	0 650	87 6	0 592
81 2	0.891	79	0.873	84	0.809	58 8	0.653	87.3	0 612
77 2	0.886	79	0 879	69	0.799			86.6	0.590
66 9	0.881	68	0.882	68	0 795			72.2	0 591
66 7	0.887	68	0.872	67	0.806			72.0	0.598
63 0	0 882	65	0 876	53	0.794			71.3	0 604
62.4	0 889	65	0 865	52	0.792			57.2	0 590
59 2	0 888	53	0 876	51	0.802			57.0	0.591
51.8	0 882	53	0.865					56 2	0.608
51.5	0 890	51	0.858					55.7	0.597
46 2	0.889	50	0.873						

BAR 14, 9.91 PER CENT. ZN

°C.	K
236.3	0.552
235.0	0.539
234.8	0.556
234.0	0.541
233.8	0.555
183.3	0.529
183.0	0.524
182.0	0.524
181.6	0.534
180.6	0.534
134.6	0.507
133.0	0.508
133.0	0.509
132.2	0.516
131.2	0.515
88.9	0.486
88.8	0.488
87.0	0.470
87.0	0.479
73.3	0.474
73.2	0.476
71.0	0.467
71.0	0.475
59.3	0.465
58.2	0.434
55.0	0.464
55.0	0.472

BAR 15, 16.76 PER CENT. ZN

°C.	K
230.8	0.459
230.7	0.458
177.9	0.436
177.3	0.434
130.5	0.415
129.6	0.413
86.6	0.394
85.5	0.404
70.4	0.384
68.8	0.395
55.0	0.374
52.9	0.386

BAR 18, 30.81 PER CENT. ZN

°C	K
238.3	0.361
182.9	0.344
132.8	0.329
89.9	0.316
72.7	0.308
56.2	0.301

BAR 16, 20.35 PER CENT. ZN

°C.	K
236.2	0.416
234.7	0.420
183.4	0.399
181.3	0.404
135.0	0.384
132.5	0.385
87.5	0.357
87.1	0.364
70.8	0.351
70.4	0.359
54.6	0.346
54.2	0.354

BAR 21, 34.53 PER CENT. ZN

°C	K
237.3	0.358
237.0	0.353
181.1	0.338
180.6	0.333
131.2	0.321
130.4	0.316
87.3	0.313
71.1	0.302
55.8	0.292

BAR 22, 40.75 PER CENT. ZN

°C	K
238.6	0.355
236.6	0.357
183.2	0.340
180.9	0.343
132.3	0.327
129.2	0.330
86.2	0.313
86.0	0.330
69.6	0.306
69.1	0.323
52.8	0.316
52.6	0.299

BAR 88, 45.02 PER CENT. ZN

°C.	K
231.6	0.379
229.0	0.381
178.7	0.379
175.3	0.379
125.9	0.378
122.2	0.377
84.0	0.360
84.0	0.367
68.6	0.361
68.5	0.367
52.9	0.363
52.9	0.367

BAR 85, 49.45 PER CENT. ZN

°C	K
234.8	0.415
232.2	0.418
183.0	0.418
179.6	0.422
130.2	0.422
126.0	0.426
86.9	0.426
86.4	0.423
86.2	0.429
71.8	0.425
71.0	0.427
70.8	0.421
56.8	0.424
55.8	0.425
55.3	0.418

BAR 52, 9.51 PER CENT. ZN 1.32 PER CENT. PB

°C.	K
217.3	0.513
217.2	0.519
164.9	0.498
164.8	0.494
116.7	0.478
116.6	0.472
72.8	0.460
70.1	0.457
59.8	0.453
56.5	0.445
47.3	0.446
43.6	0.433

BAR 54, 37.88 PER CENT. ZN, 2.01 PER CENT. PB

°C	K
227.3	0.331
225.8	0.328
171.0	0.313
169.6	0.310
120.5	0.297
119.2	0.294
83.3	0.282
82.6	0.278
65.3	0.275
64.8	0.273
48.2	0.268
47.0	0.268

BAR 55, 18.63 PER CENT. ZN, 0.20 PER CENT. SN

°C.	K
242.2	0.424
184.2	0.403
131.8	0.383

BAR 56, 27.77 PER CENT. ZN, 1.02 PER CENT. SN

°C	K
234.5	0.338
234.2	0.336
176.9	0.319
176.9	0.317
125.4	0.302
125.6	0.300
84.0	0.285
65.4	0.279
47.8	0.272

BAR 57, 39.36 PER CENT ZN, 0.70 PER CENT. SN

°C.	K
244.0	0.330
232.9	0.329
231.5	0.330
183.4	0.315
175.3	0.314
174.4	0.315
128.2	0.301
122.7	0.300
122.2	0.301
82.8	0.292
82.7	0.296
64.8	0.287
64.6	0.291
47.3	0.283
47.3	0.286

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DISCUSSION

O. W. ELLIS, Toronto, Ont.—This paper is particularly interesting because it is only recently that the importance of measurements of thermal conductivity in these copper-base alloys has begun to be realized. This is especially true in electrical engineering, where the possibility of increasing the strength of certain alloys for parts of electrical machinery is to some extent precluded by the fact that every increase in strength is accompanied by a reduction in electrical conductivity on the one hand and in thermal conductivity on the other.

It is rather interesting to realize that in certain situations it might be possible to use alloys having relatively low electrical conductivities, were it not for the fact that their thermal conductivities are also low. For example, take the case of commutator bars for electrical machines. I think it may be said definitely that successful endeavors to increase the strength of such bars have been made, and that the electrical conductivities of the alloys tested have been considered entirely satisfactory, but that the thermal conductivities of the alloys were below the figures required. Any work, therefore, that Dr. Smith can do along these lines is worth while.

I was interested in the apparatus employed for the conductivity measurements. I do not wish to suggest that he should alter this apparatus, because I know the amount of time that must have been expended in making it, but I know that in certain experiments that we carried out on the conductivity of copper and certain copper alloys we found it desirable to duplicate the apparatus, as it were—in other words, to carry the test bar through on both sides of the center heating coil, so that measurements could be made on either side of the coil without the necessity for duplicating experiments.

C. S. SMITH,—Before building the apparatus used in my tests, I made a study of all types that could be used, and adopted the present form as best for my particular purpose. The double-ended form mentioned by Mr. Ellis is preferable when the

heat *input* is measured electrically, but the best results are obtained only when the heating coil is completely embedded in the specimen, to prevent any lateral loss of heat.   This necessitates a test bar so intricately machined that it would not be practical in the present case.   When the heat *removed* is measured by using a water-flow calorimeter at the cold end of the bar there is no advantage, other than a slight saving of time, in using the double-ended apparatus, and the difficulties of construction become greater.

Causes of Cuppy Wire

By W. E. Remmers,* Chicago, Ill.

The defect in wire known as "cuppiness" has appeared and disappeared from time to time but the exact cause of its appearance or disappearance has not heretofore been known definitely. This defect is not limited to one particular metal or alloy but seems to be found at various times in all of the materials that are drawn into wire. Fig. 1 represents cuppy wire made from an aluminum alloy and Fig. 2 illustrates copper wire that became cuppy in drawing without intermediate annealing.

Differences of opinion are current among the manufacturers of wire and in the literature (see bibliography at end of paper), some believing that the source of the trouble lies in segregation in the wire rod, oxides, sulfides, slag, etc.; others that the trouble is created by an unevenness of stress distribution across the section of the wire, usually thought of as being a function of die shape. All of the published work is of a qualitative rather than a quantitative nature. With this in mind, it was deemed advisable to make a study of the shape of the wire-drawing dies, as well as the oxygen content of the copper to be drawn.

EXPERIMENTAL

After several methods were tried, it was found that by studying the contour of the butt-end of the rod after drawing a measure of the "working" across the section of the wire could be made. The butt-end of the annealed rod was not sheared but was sawed off. The end was then smoothed with a fine file so that the plane of filing was perpendicular to the drawing axis. It is to be noted that this method is not an absolute measure of the distribution of cold working but is a very good indicative means of studying comparative values.

The method of examining a tension break in wire was found to be the most sensitive in detecting cuppiness. Other methods, such as microscopic examination of longitudinal sections, X-ray radiographic studies, etching away of outer layers with nitric acid, and fracture by bending, can all be used to identify cuppy wire but the tension break will give the fracture characteristic of cuppiness before any of the other methods can

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* Metallurgical Engineer, Western Electric Co., Inc.

detect it. Close examination of the surface will frequently reveal cuppy wire but there is a slight possibility that the surface undulation is due to a relatively large non-metallic inclusion.

When copper wire is in such a condition that none of the usual tests, except a tension break, reveal cuppiness, it can frequently be retrieved by annealing. This is a condition slightly anterior to the stressing to internal rupture.
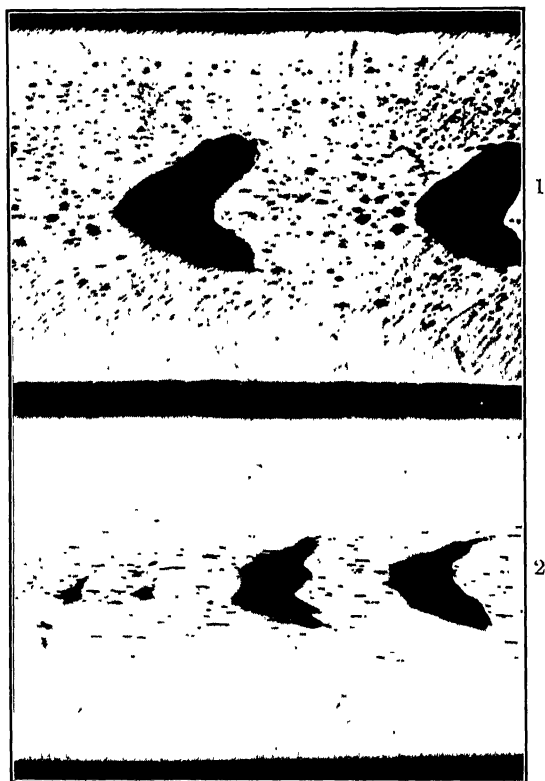
FIG. 1.—CUPPINESS IN DURALUMIN WIRE. ✕ 66. NaOH ETCH.
Reduced in four dies from No. 17 (0.045 in.) to No. 21 (0.028 in.) B. & S. gage.
FIG. 2.—COPPER WIRE REJECTED BECAUSE OF CUPPINESS. ✕ 22. HNO₃ ETCH.
Reduced in eight dies from ¼-in. rod to No. 12 (0.081 in.) B. & S. gage.

Among the various conditions studied were straight-sided and curved die contours, amount of reduction per die, the effect of a lubricant, relieved dies, and oxygen content of the copper. Copper rod of the following oxygen contents was used: 0.019, 0.042, 0.139 per cent. The 0.042 per cent. oxygen rod is representative of the usual oxygen content of copper wire, the other two are considered extremes.

Straight-sided dies with the included angles varying from 4° to 90°, and with all of the reduction accomplished in a single angle, were used in drawing the three grades of copper rod. It was found that as the angularity of the die increased, the depth of the butt-end cone increased. This concavity increased until in the extreme cases the wire became badly cuppy in the few dies used, Figs. 3 to 7.

Several sets of dies were made with the radius of curvature on longitudinal section ranging from $\frac{1}{16}$ to $2\frac{1}{2}$ in. The results follow closely
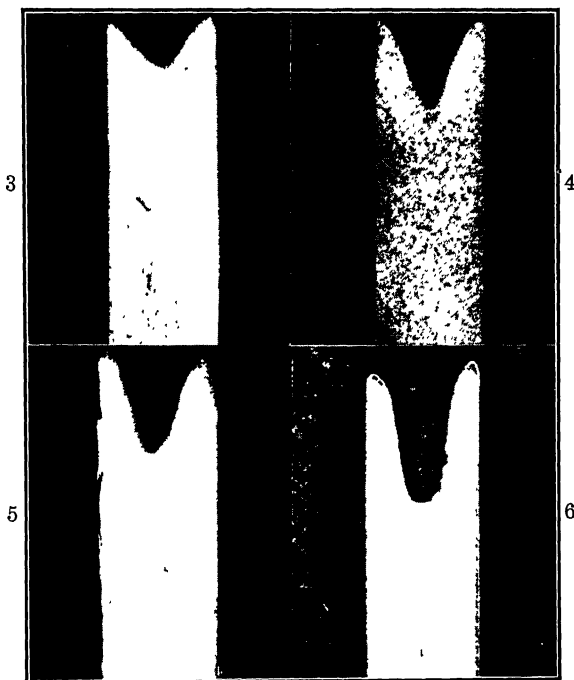
FIGS. 3 TO 6.—COPPER ROD OF 0.042 PER CENT. OXYGEN CONTENT DRAWN THROUGH DIFFERENT DIES.. LUBRICANT WAS USED IN ALL THESE DRAWS.

Fig. 3.—Drawn through 4° included-angle dies.
Fig. 4.—Drawn through 8° included-angle dies.
Fig. 5.—Drawn through 18° included-angle dies.
Fig. 6.—Drawn through 40° included-angle dies.

those obtained from experiments in varying the straight angle. The smaller the radius, the nearer the wire approached to a condition of cuppiness. By comparison with the indentations on the end of straight-angle drawn wire, the "effective angle" of these dies can be estimated.

A method was devised for recording the longitudinal section through a die without ruining the die for further service. A 30-in. pantograph was mounted on a drawing board with the pencil in the large-motion position and a tapered needle bent 90° in the small-motion junction.

This needle carried a T-shaped head. The metal die was supported by clamping to a small iron bracket. It was necessary to center the die by running the needle through the die opening until contact was made all around. The die was then fastened in that position. To determine when contact was first made between the needle and die, it was necessary to connect the needle and the bracket supporting the die to the open ends of a buzzer circuit. As soon as the contact was made a sound was produced. The pantograph was operated from the pencil end by recording a series of contact positions rather than attempting to trace directly the die contour. An example of the graph is shown enlarged in Figs. 8 and 9. It should be noted that, on account of the width of the head
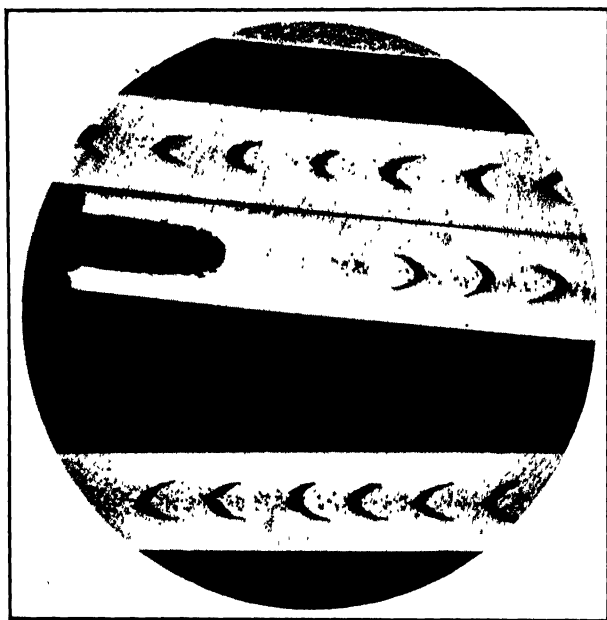
FIG. 7.—COPPER ROD OF 0.042 PER CENT. OXYGEN CONTENT DRAWN THROUGH 50° INCLUDED-ANGLE DIES. LUBRICANT WAS USED.

of the T, orifice diameters are not magnified to the same extent as the other dimensions of the die.

The influence of the oxygen content of the copper was investigated to determine its role in producing cuppiness. High oxygen has been considered as an aggravating factor but to what extent its influence was exerted has not been previously determined according to published information.

The portion of the rod used in the laboratory experiments was 0.146 in. dia. and was annealed. The size of finished wire was 0.081 in., having been reduced in five draws through dies of the following sizes: 0.133 in.,

0.115 in., 0.102 in., 0.088 in. and 0.081 in.   In some of the mill experi-
ments the wire was drawn as fine as No. 22 gage.   The rods of different
oxygen contents resulted in cuppy wire when drawn through dies of
different included angles, which presents the fact that the effect of oxygen
as an aggravating factor in the production of cuppy wire might be
measured in degrees of die angle (Fig. 10).

The solid-line curve is for the five draws used in these experiments
and not for any number of reductions.   By further reduction of the wire
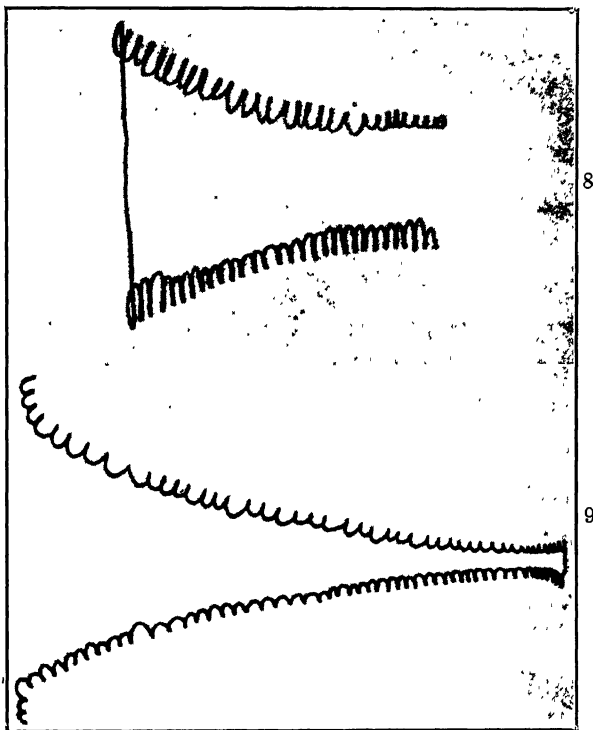
FIG. 8.—PANTOGRAPH RECORD OF SHAPE OF 0.157-IN. DIE.   × 16.
FIG. 9.—PANTOGRAPH RECORD OF SHAPE OF 0.072-IN. DIE.   × 16.
(Both reduced 25 per cent.   Original magnification given.)

to finer sizes, the solid-line curve, as shown, will be moved considerably
to the left, somewhere in the region of the dotted lines.   The positions
of these dotted lines were approximated by the results of experiments
made in the mill and by interpolation.   These positions are not estab-
lished with the same degree of accuracy as that of the solid-line curve.

The usual reductions as used in production were compared with
larger and smaller reductions.   The usual reduction was accomplished
in dies of about 20 per cent. reduction in cross-sectional area for each
draw.   The average amount of reduction was increased to 33.0 per cent.

in one set of dies and decreased to 13.5 per cent. in another, the die angles being held constant in each experiment. It was noted that the larger the reduction per die, the more uniformly distributed will be the cold working of the metal and with that greater remoteness from a cuppy condition.

A study of the effect of the so-called lubricants was made to determine the effect, if any, upon the distribution of cold working across the section of the wire. A comparison was made by drawing with and without lubricant. The lubricant was the same beef-tallow soap emulsion used in production and was heated when used in these experiments. There was no measurable difference between the two indentations.

Turpentine, with its decided anti-lubricating properties, was then tried instead of the lubricant, and even though the pull on the die increased somewhat, the difference in butt-end indentation was slight. From this
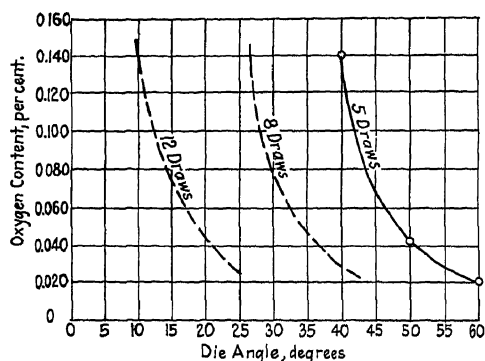
Fig. 10.—Relationship between effective die angle and oxygen content of copper. Wire is cuppy to right of curve.

one might say that the influence of the lubricant in determining the distribution of working is almost negligible, considering lubricating properties alone.

Several draws were made to see if a relieved die was to be more desired than the abrupt discharge that is frequently found in chilled-iron wire-drawing dies. These dies were relieved by straight angles and by smooth radius curved surfaces. It appeared that a relieved die tends toward a deeper indentation which, of course, indicates an undesirable condition. A slight increase in power consumption was also recorded. The results are similar, both for straight-sided dies and smooth-curved dies.

By reversing the wire each time it was drawn through successive dies, one might think that perhaps some of the deleterious effects of wide-angle dies would counteract the effect remaining from the previous draw, since the direction was reversed. In all cases where the direction of drawing
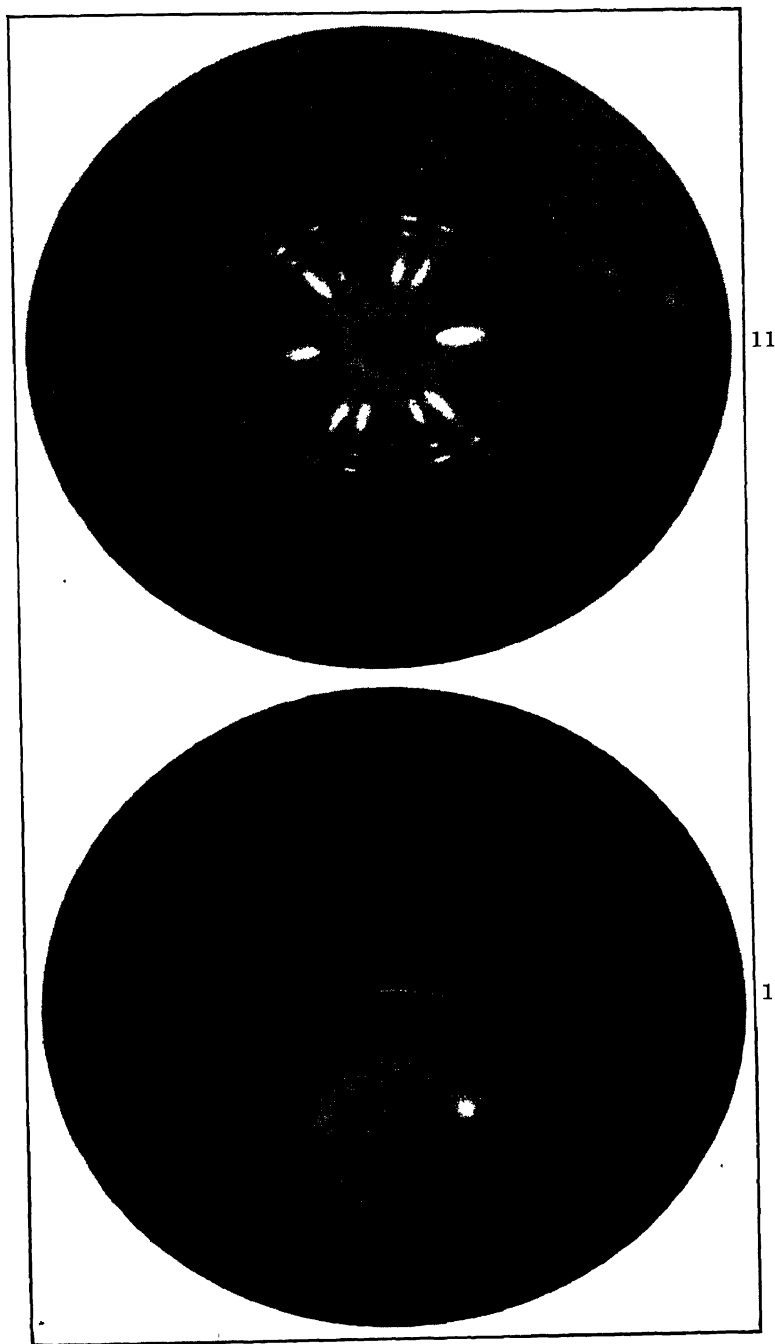
FIG. 11.—PATTERN OF CORE OF 0.081-IN. CUPPY WIRE.
FIG. 12.—SURFACE PATTERN OF 0.081-IN. CUPPY WIRE.
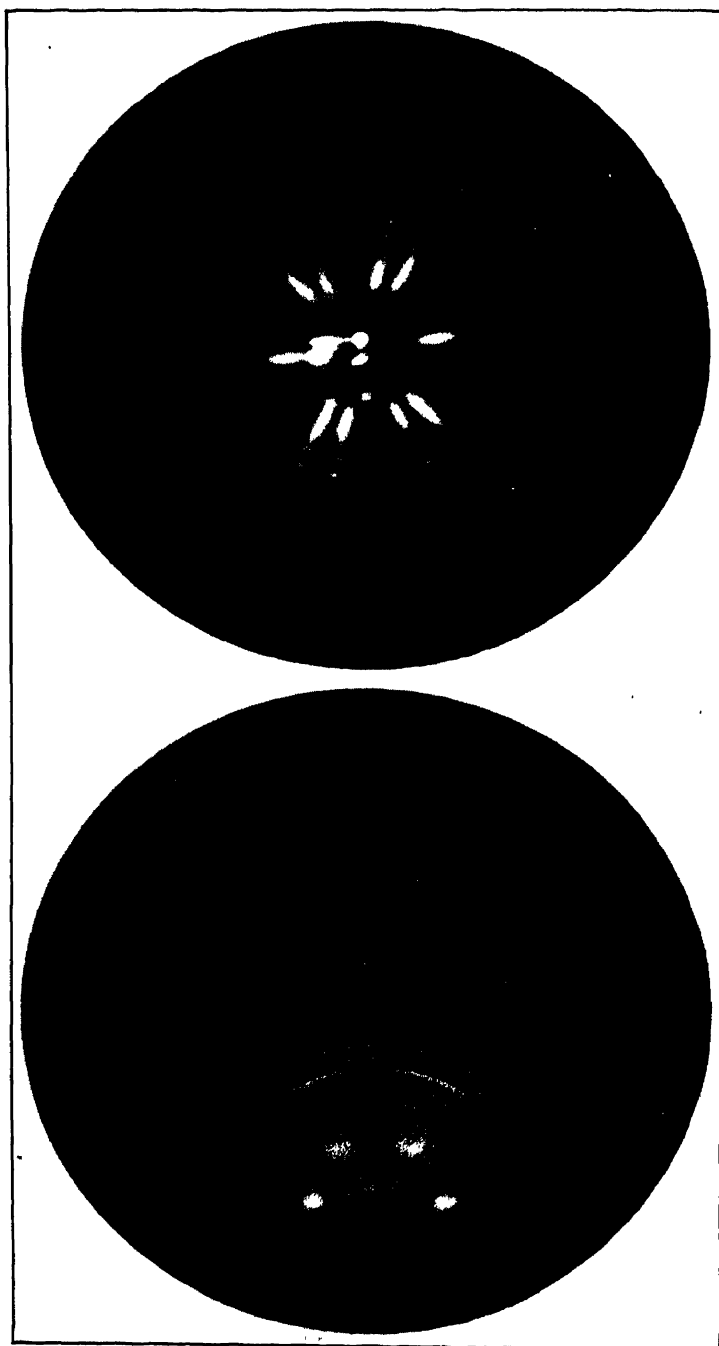
FIG. 13.—PATTERN OF CORE OF 0.081-IN. GOOD WIRE.
FIG. 14.—SURFACE PATTERN OF 0.081-IN. GOOD WIRE.

was changed, the copper became cuppy one die earlier than if a single direction had been used. This cup is characteristic of genuinely cuppy wire.

Numerous new and used chilled-iron dies were examined. These dies were reamed with two straight-edged reamers to form the working section of two conical surfaces. In many of the new dies the axes of the two conical shapes were not coincident, making the die contour a shape composed of two oblique conical frustra instead of right conical frustra. This obliquity results in an elliptical wire instead of a circular one, as well as an eccentricity of reduction. This is also apparent in the butt-end identation of wire drawn through this type of chilled-iron die.

In the discarded dies an annular groove is noted in almost every die just at the point of contact of the copper. The formation of the groove rapidly increases the abruptness of reduction but within the usable limits the effective angle of the die is slightly decreased. This can be explained by the wearing away of the sharp angular junction between the approach and the land, resulting in a smooth-curve reduction. The presence of reamer marks in the new dies contributes also to the difference of effective angles.

The fact that the so-called "good" wire produced from these dies is in a condition very similar to that of the cuppy wire can be seen in the four X-ray patterns shown in Figs. 11, 12, 13 and 14. The corresponding patterns from the outside and from the inside of the good and the cuppy wire are almost identical. This means that the good wire examined is in a highly strained condition, with a definite orientation at the core but almost no regular order of crystals at the surface. In the most desirable condition, orientation should be apparent in surface of the wire as well as the core.

SUMMARY

There is a definite relationship between the die angle and oxygen content of copper wire rod, which determines whether or not the rod can be drawn into good or cuppy wire. This relationship can be altered by various factors, smooth-curve contour dies and large reductions per die acting to give a better product while relieved dies, reversals of drawing direction and many reductions tend to make a product of lower quality.

ACKNOWLEDGMENTS

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DISCUSSION

K. R. VAN HORN, Cleveland, Ohio.—We have observed cuppiness in aluminum wire, particularly in duralumin, 17ST. It is easy to detect this condition by means of radiography. I wonder if Mr. Remmers has considered this method. The internal V-shaped fractures are less dense than aluminum and therefore readily discernable.

At first, we wanted to attribute the difference in properties in the core and exterior surface to a difference in orientation; i. e., core possessing an orientation more favorable for slip. A cuppy duralumin wire drawn 44 per cent. showed random orientation in both sections. The discrepancy between our random orientation and Mr. Remmers' highly preferred pattern is accounted for by merely a difference in the amount of reduction.

We also pulled the outside surface as a cylinder and the inside core as a rod and found a higher tensile strength and lower elongation in the outer surface than in the core. We seem to think that the die angle has a marked effect on the cuppiness of our wire.

W. A. SCHEUCH, Chicago, Ill.—Mr. Remmers' presentation of the causes of cuppy wire gives us a quantitative measure of what we may expect from some sources. I believe the title of the paper should be "Some Causes of Cuppy Wire."

Copper wire mills may suddenly begin producing cuppy wire and then just as suddenly stop, without changing either dies, brand of copper, or even furnace lots of copper. Recently we had a case of very cuppy wire in our mill, and naturally, on the basis of data which Mr. Remmers found, the reaction was to change the copper. In changing the copper, other things were changed, and the combination of changing factors immediately produced good copper. Good copper having been produced from other copper, the copper that was classed as no good was immediately thrown back into the mill, and that likewise produced good copper wire without cuppiness. I believe that there are other possible causes of cuppy wire and our engineers are conducting studies along these lines.

E. S. DAVENPORT, Bloomfield, N. J.—I have seen one case of cuppy wire in drawn tungsten. As it was not a pressing problem at the time, it was not followed down. The cup was so pronounced that the wire fractured and one portion of it was simply a tube. It was possible to look down into the center of the wire for a considerable distance.

Mr. Remmers' pantographic method of studying die contours is interesting. I have had some contact with a similar problem in studying some cold-drawing dies. An attempt was made to establish some method of determining the die contours in order to arrive at the most desirable shape. One method is to cast impressions of the dies and then project silhouettes of them on to a screen carrying an outline of a standard contour. I do not know whether the method has any real merit or not, but I believe that the contour shapes shown by Mr. Remmers are more accurate.

S. L. HOYT, Schenectady, N. Y.—This paper suggests many questions. One point that comes to my mind relates not so much to the operating conditions that are responsible for cuppiness as to the mechanism of deformation that gives cuppiness. For instance, the cup has a definite shape—conical—and I wonder if that is due to a fracture such as would be obtained in a tensile test, or if the shape of the cuppiness is due merely to the flow of metal as the wire is passing through the die.

The problem, I believe, could very well be attacked from another angle. The cuppiness, as Mr. Remmers has pointed out, and as is well known, gives a series of internal fractures which are evenly spaced. There must be some reason for the particular type of spacing. If that reason, which is certainly a striking phenomenon, could be closely ascertained, I am sure that we would be closer to the true causes of cuppy wire. I would like to ask Mr. Remmers if he is considering work along lines that would deal with the deformation of the metal during drawing, as an approach to the solution of this problem.

E. A. ANDERSON, Palmerton, Pa.—Zinc, which recrystallizes at a lower temperature, also has an erratic grain structure at times, some coarse and some fine. In drawing an extruded zinc alloy rod, we ran across a phenomenon very like cuppiness in wire. On polishing a section of the rod, we found that the outer layer, which had held together, was fine grained and the inside was very coarse. It was evident that the original, well-annealed extruded rod, in going through a slight drawing operation had hardened on the surface sufficiently to recrystallize, but had not hardened on the inside and had left the coarse-grained inner structure which will not stand the stress of drawing and had become strong enough outside to hold it together.

In this case the deformation had not gone far enough to remove the straight-line fracture. That is, the fracture was at right angles to the direction of drawing and had not pulled into the cone shape. In answer to Dr. Hoyt's question, I think that possibly the fracture occurs at an early stage of the drawing and merely pulls around into the cone shape later. Copper may do the same thing, as there may be sufficient difference in the stress on the outside and the inside to alter the annealing characteristics.

J. L. CHRISTIE, Bridgeport, Conn.—I have had the same experience described by Mr. Anderson. I saw some zinc drawn which had previously been extruded. The extent of the cuppiness was so great that the wire, after it came out of the die, looked like linked sausages. Not only had it fractured in the center, but had necked down. The sausages themselves were of fairly uniform length, but not so uniform as the fractures shown in the photomicrographs. We concluded, just as Mr. Anderson did, that the working had rendered the outside sufficiently ductile to stand the draw, whereas the amount of working had not been sufficient to penetrate completely through and make the central core sufficiently ductile.

E. A. ANDERSON.—We did not need to etch the structure of our rod or polish it in any way. The rod was about 1 in. dia., and the fracture was easily ⅛ in. across between the walls of the fractured portion.

W. E. REMMERS.—Mr. Van Horn brought up a question on radiographic X-ray work on cuppy wire. We have done some of that work but have encountered several

difficulties because of the fine gage of the wire, No. 22. This method of inspecting samples was discarded because more satisfactory methods of detecting cuppiness were found before sufficient X-ray technique was developed to produce consistently good results. It is reported by G. L. Clark[1] that detailed radiographs of cuppy aluminum rod have been obtained. The size of his rod is much larger than the copper wire with which we worked. The fact that aluminum is relatively less dense with respect to X-ray penetrability may also assist in the operation of securing good detail in radiographs.

Perhaps Mr. Scheuch is correct in his remark concerning the title. Originally it was "A Study of the Causes of Cuppy Wire" but in the condensing previous to publication, the first few words were dropped. It is possible that other causes of cuppiness exist.

The method of casting a form of the die and then projecting the outline on a piece of drawing paper, mentioned by Mr. Davenport, was tried. We used plaster of Paris and one of the low-temperature "fusible" alloys. In using a Bausch and Lomb projection machine the heat of the beam of light fused the form of fusible alloy when the sketcher was not rapid enough in producing the outline of the die. This method of determining die contour is satisfactory for new dies, but in used dies where an annular groove is worn into the die or where imperfections exist, such as a pitted surface, this method does not give the important details. The protruding sections of the form are sloughed off in extracting it from the die.

Dr. Hoyt brings up the subject of causes for such a characteristic shape for this fracture. In copper wire, I have never seen fractures of any other shape. This would indicate that the characteristic shape is produced at the time of forming the discontinuity. This same shape is characteristic when reversing the direction of drawing with each reduction and producing cuppy wire. In some other metals in which cuppiness appears, I understand that conditions are different.

Ordinarily, all of the cups point in the same direction along the core of the wire, but in one instance in duralumin wire an internal fracture appeared to be a pair of cups opposite in direction. I would hesitate to say that this fracture actually contained a reversed cup. It may have been the result of some critical condition at that point, such as heterogeneity of the metal or an inclusion that diverted the tearing from its normal course.

Concerning the link sausages in drawn zinc, described by Mr. Christie, the same general condition of lessened diameter of the wire is noted in copper. This condition, described as a series of undulations in the surface of the wire, exists to a much smaller degree in copper; it can be detected by drawing the wire carefully between the finger tips.

S. L. HOYT.—I am interested in Mr. Davenport's remarks regarding cuppiness in tungsten wire. Tungsten wire, of course, in its ductile condition is definitely fibrous, whereas copper wire, while fibrous, does not approach the condition common in tungsten wire. Evidently cuppiness in tungsten wire is not common.

E. M. WISE, Bayonne, N. J.—In connection with Dr. Hoyt's speculation on the mechanism of the formation of these cups, I would like to ask whether there was any change in the character or in the existence of such cups in wire that was drawn under tension—that is, in a manner analogous to rolling under tension, a method which would reduce the pressure on the die wall—and also whether the situation was changed materially when swaging was substituted for drawing? That is departing somewhat from the text of the paper, nevertheless it is such a fundamental matter, for cuppiness

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[1] G. L. Clark: X-ray Metallography in 1929. *Metals and Alloys* (1929) 1.

is encountered in drawing steel and other materials, that it is interesting to speculate regarding other possible methods of reduction.

W. E. REMMERS.—The tension drawing is being tried in a series of experiments utilizing the reverse tension drawing. As yet we have not drawn enough wire to begin on the investigations of cuppy wire along these lines.

K. R. VAN HORN.—Relative to the application of radiography to these specimens; probably the specimen of aluminum referred to by Mr. Remmers was given in Mr. Clark's article,[2] in which he showed definite V-shaped fractures in 0.25-in. aluminum wire. It is possible to detect small voids in 19-gage aluminum wire with exposures of the order of $\frac{1}{2}$ to $\frac{3}{4}$ min. Certainly, it would be easy to find cuppiness in copper wire which would be of a considerably larger order of magnitude than the small voids mentioned above. Perhaps the copper would require a somewhat longer exposure, but I think would not require over 1 min. or perhaps $1\frac{1}{2}$ min. exposure with a tungsten tube, 70 kv., 6 ma. It is, however, important that the wires should be in close contact with the cassette.

W. A. SCHEUCH.—Regarding the question of whether cuppiness is due only to the causes specified in the paper, the method of investigation by which this was approached by Mr. Remmers was anticipated by the engineers. The latter actually took a bar, as I recall, and cut it in half. They treated one-half in a reducing atmosphere, put it through the dies, and followed it up with the other or untreated half, using the same dies and the same machines. One-half became cuppy and the other half did not do so. I see no reason why this does not indicate that there are other possible causes, perhaps epually important from the manufacturing standpoint, which produce cuppy wire.

W. E. REMMERS.—In all probability cuppiness in copper wire can be detected by radiographic methods. With copper wire, it is much easier and more rapid to merely bend the wire or fracture it by a tension pull.

The experiment described by Mr. Scheuch affirms rather than contradicts the conclusions of the paper, which state that oxygen is effective in producing cuppiness. A paper was published several years ago by Mr. Bassett and Mr. Bradley,[3] which shows the way in which oxygen is removed from the surface of copper when exposed to reducing gases. It is possible that the same thing was taking place in the wire bar heated in a reducing gas in Mr. Scheuch's experiment. From the conclusions as reported in the paper, the low-oxygen surface material of wire bar should draw differently from the oxygen-rich core.

MEMBER.—In regard to the oxygen content, the determination of which I understand was estimated from the microstructure, did the author make note of the condition of the oxide particles, as to size and distribution, and has he done any work on the effect of the oxide particles on the size and distribution of the cuppiness that is produced?

W. E. REMMERS.—We have made no study of the size of the oxide particles in cuppy wire. The figures given for the oxygen content are those reported by our chemical laboratory. We used the microscope only as a check on the chemical laboratory when the determinations were made on the cast wire bar.

S. L. HOYT.—As a method of studying the causes of cuppy wire, it would be interesting to try wire composed of two metals; that is, a core of hard metal and a surface

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[2] G. L. Clark: *Op. cit.*

[3] W. H. Bassett and V. C. Bradley: Action of Reducing Gases on Heated Copper. *Trans.* A. I. M. E. (1926) **73**, 755.

of soft metal, and then the reverse condition. In the photographs of cuppy wire, it is evident that the core is behaving in a different manner from the outside. Is that due to a different condition of strain, or is it a condition that is irrespective of the condition of the metal?

W. E. REMMERS.—We have made surface diffraction patterns of copper wire, starting with it as drawn wire with the surface etched off slightly and continuing etching until we obtained a fine wire. Strange as it may seem, our patterns are very similar to those reported in the discussion of the paper by Sykes and Ellsworth.[4] We find a decided change from random orientation on the outer surfaces to more or less oriented condition as we approach the center of the wire. Further than that, we have made no study of strain except that on the butt-end of the copper wire.

S. L. HOYT.—One wire of the type I mentioned is copper-clad steel wire, commonly called "Dumet wire." Can anyone tell us if cuppiness is at all present in the drawing of Dumet wire? It may be something more like tungsten wire, material that does not cup.

W. K. FRANK, Glassport, Pa.—Our company has been manufacturing, for the past 15 years, a wire composed of a steel core to which a copper cover has been molten-welded. Cuppiness is produced in a wire of this type either by overdrafting or by shrinkage or segregation in the steel ingot from which the steel bars were produced. It would appear that internal weaknesses in any material will produce cuppy wire, and it would be well to investigate the soundness of copper wire bars with particular relation to oxygen content and pouring temperatures. Cast materials are weakest at the last point of freezing. The amount of shrinkage in copper, of course, is dependent on the oxygen content and pouring temperature, or most particularly on the rate of cooling.

S. L. HOYT.—The copper in your wire is on the outside?

W. K. FRANK.—Yes. The cause of cuppiness can generally be traced to segregation of the original steel ingot. The shrinkage in the steel as cast has produced a weakness in the core of the steel, which later fractures and causes cuppiness. We can also produce cuppiness by overdrawing wire; simply by drawing to a point where it fractures.

S. L. HOYT.—You say you can produce cuppiness by overdrawing it, but is not cuppiness evidence of overdrawing, and does not cuppiness occur in some wire at different degrees of reduction? You seem to put the cart before the horse.

W. K. FRANK.—By the term "overdrawing" I mean putting cold work on a given material beyond which normal material should not be worked. I feel that material that develops cuppiness with a normal amount of cold work is usually a material that has internal weaknesses caused either by segregation or shrinkage in the original cast.

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[4] W. P. Sykes and A. C. Ellsworth: On the Distribution of Hardness Produced by Cold Working. Amer. Soc. Steel Treat (1929).

Certain Types of Defects in Copper Wire Caused by Improper Dies and Drawing Practice

By H. C. Jennison,* Waterbury, Conn.

Two distinct types of defects occur at times in copper wire as a result of the use of dies of improper design or undesirable wire-drawing practice. The conditions under which these defects may be produced, as well as precautions to be taken in order to prevent them, have been known to The American Brass Co. for many years. The quality of the copper wire bars and rods has too often and unjustly been held responsible for these particular defects and it is to correct any such belief that this paper is presented.

An extremely high quality of electrolytic copper has been supplied to the trade by all refineries for the last 20 years at least. The purity of the copper would average well above 99.900 per cent. The casting of the wire bars has been handled in a generally satisfactory manner. The bars have been cast sound, with a flat to slightly crowning set and have been free from sloppy edges, cold sets, etc. In other words, the wire bars have met A. S. T. M. specifications and have been generally satisfactory. For the most part, they have been everything that could be desired from a quality standpoint yet most of the wire mills in this country and in Europe have at times held the quality of the copper responsible for the two types of defects described in this paper. As a matter of fact, these defects are produced entirely in the wire mills. The author has visited many of the large wire mills in the United States and in Europe to investigate these defects. In some cases the trouble has been so serious that the wire mill has ceased operations.

At times the wire mills are reluctant to believe that they are responsible for the defective product. The effect of die design, wire-drawing practice, etc., upon the quality of copper wire has received little study on the part of wire mills, particularly those that have commenced operations in the last few years.

Two Types of Defects

One type of defect is generally known in this country as "check marks;" in Europe it is termed "crowfeet" (Fig. 1). This defect occurs in the surface of the copper wire, in the form of V's, which are always

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found in a line and point in the direction of drawing. Wire affected in this manner is brittle and can be broken easily when bent at one of the check marks.

FIG. 1.—CHECK MARKS (CROWFEET) IN SURFACE OF COPPER WIRE.

Another type of defect is known as "cup and cone" wire or "cuppy" wire. This defect is internal. When the wire is broken in tension or by bending the characteristic cup and cone break is obtained. Fig. 2 shows one-half of a fracture. It resembles a small tube. The two halves of a similar break are shown in Fig. 3. The cone always points
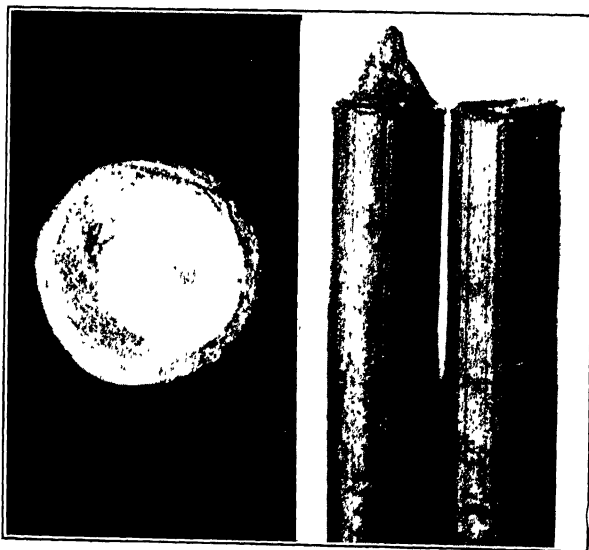
FIG. 2.—END VIEW OF FRACTURE CAUSED BY CUP AND CONE DEFECT.

FIG. 3.—BOTH HALVES OF BREAK [SIMILAR TO THAT IN FIG. 2.

in the direction of drawing. Wire affected in this way is also brittle and will break easily when bent.

The defects described may be produced or prevented at will by following the details outlined in the following pages.

DIE DESIGN IMPORTANT

Die design plays an important part in the defects described. Dies for drawing copper wire are cut principally from chilled iron blanks cast especially for this work. Fig. 4 illustrates in detail a typical chilled iron die of proper design. It will be referred to frequently throughout this paper. This figure shows particularly three parts of the die. Bell A is not used for drawing wire. The chilled iron in this area is simply cut and made smooth so as not to tear the copper entering the die in case it should touch or drag on the sides. The first drawing stage of the die is bell B and the next step is known as the bearing.

No attempt was made in this investigation to study the flow of metal in the dies. One familiar with the art of wire drawing will appreciate the difficulties this problem presents.
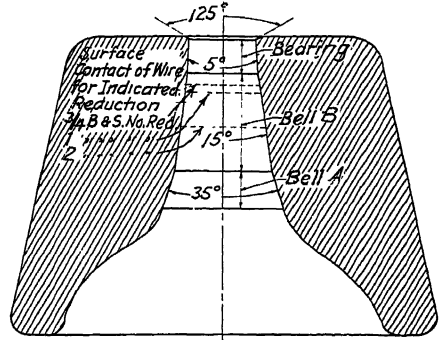
FIG. 4.—TYPICAL CHILLED IRON DIE OF PROPER DESIGN WHICH WILL NOT PRODUCE CHECK MARKS EVEN WHEN OLD.

CHECK MARKS

This type of defect has been overlooked by most investigators. Check marks are the result of a certain type of tear or rupture in the
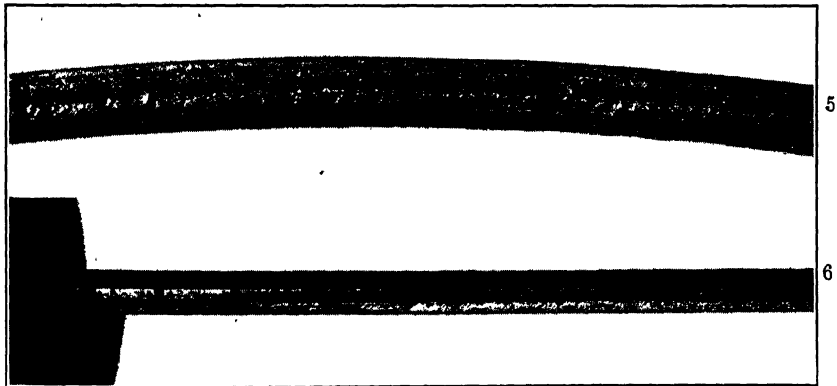
FIG. 5.—BEGINNING OF CHECK MARKS IN TORN SURFACE OF COPPER WIRE CAUSED BY ENTERING DIE ECCENTRICALLY.
FIG. 6.—SAME WIRE AS IN FIG. 5, DRAWN TO SMALLER SIZE.

surface of copper wire, which occurs usually as the wire is being drawn. As the drawing is continued, particularly if under adverse conditions, the ruptures take their characteristic V shape, Fig. 1, and point in the

ection of drawing.   Additional drawing will make the wire extremely
ttle at these defects or surface ruptures and finally further drawing
:omes impossible.   While the defects occur in line, they do not extend
m end to end in the wire but are found in short stretches about 3
long, or less.   The reason for this will be explained later.   The
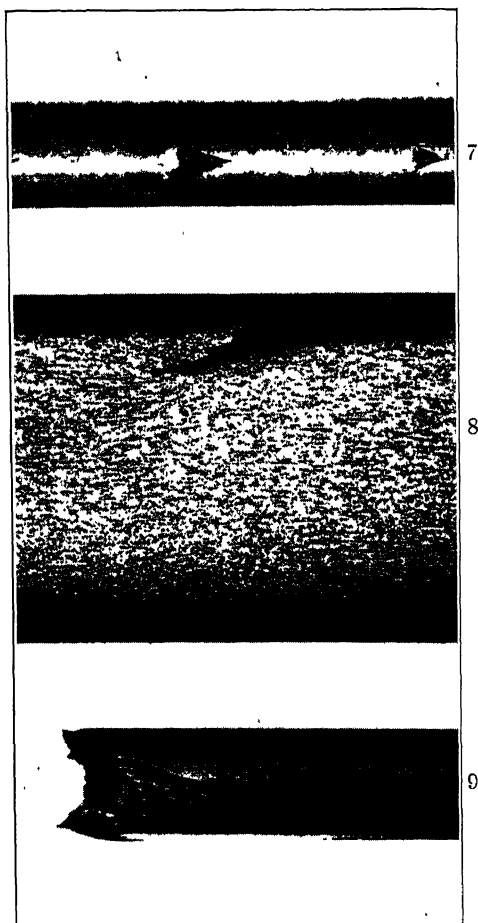
FIG. 7.—SAME WIRE AT HIGHER MAGNIFICATION.
FIG. 8.—LONGITUDINAL SECTION THROUGH CHECK MARK.
FIG. 9.—TYPICAL FRACTURE OBTAINED ON BENDING WIRE AT CHECK MARK.

rface of the wire will become torn or ruptured and check marks will
sult if the angle at bell B, Fig. 4, is great, particularly if the wire does
t enter the die concentrically.
   Fig. 5 shows the manner in which copper wire has been torn as the
sult of entering eccentrically a die of rather great angularity.   In other
ords, the longitudinal axis of the wire in entering the die did not coincide

with the longitudinal axis of the die. The surface has been torn or ruptured badly and the beginning of check marks can be seen easily. Fig. 6 shows some of the same wire drawn to a smaller size. The V-shaped defects point to the right, the direction of drawing, and may be seen easily. Sometimes these defects are in the form of sharp V's, as illustrated in Fig. 6; frequently they take more of a rounded shape, depending upon the amount of drawing, shape of dies, etc. Fig. 7 shows some of the wire at higher magnifications; the defects are seen more distinctly. Fig. 1 shows a defect in a certain area at a still higher magnification. Fig. 8 is a longitudinal section taken through one of the defects and illustrates the manner in which the wire is torn or ruptured below the surface. Fig. 9 shows well the typical fracture obtained on bending the wire at one of the defects.
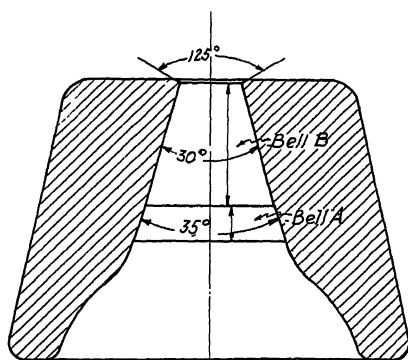
FIG. 10.—DIE WITH 30° BELL AND NO BEARING, WHICH WILL ALWAYS PRODUCE CHECK MARKS.
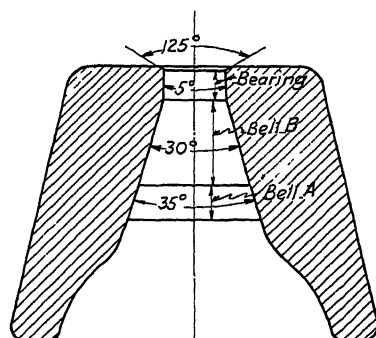
FIG. 11.—DIE WITH 30° BELL AND A BEARING, WHICH WILL NOT PRODUCE CHECK MARKS WHEN DIE IS NEW.

Check marks are elusive and frequently it is difficult to find the exact source of trouble without spending considerable time studying the problem. It is safe to say, however, that check marks indicate that the copper wire is in some way being torn at the surface. The principal source of such trouble is the die design. A die of great angularity at bell *B* with a short bearing or no bearing at all, particularly when the wire is receiving heavy reductions in drawing, will cause check marks rapidly. For example, dies having a 30° bell and no bearing (Fig. 10) will produce check marks as soon as they are placed in operation. On account of the absence of a bearing, the wire is not held concentrically in the die. On continuous wire machines the wire will whip back and forth in the die and the surface of the copper will become torn at points where this whipping action is greatest. This is the reason that check marks do not occur from end to end in wire, but in stretches. A die with a 30° angle at bell *B* and with a bearing (Fig. 11) will not produce check marks when first placed in service. The bearing holds the wire

concentrically in the die, eliminates maximum whipping action and consequently prevents the formation of check marks.

Dies in which the drawing surfaces are not smooth, because of blow-holes, plugging with scale, etc., are likely to tear the surface of the copper wire and cause check marks. The surface of copper wire may be drawn across parts of machinery, equipment, etc., and be torn.

Frequently wire mills feel that it is economy to keep the dies in operation as long a time as possible. Under such conditions, the original design of the die is destroyed and irregularities may occur that will tear the wire and produce check marks. Frequently, new dies may produce wire of satisfactory quality but after the dies have been used for a short time, the wire breaks as the result of check marks. This indicates that the dies were not of the proper design, although they did not produce check marks immediately.

It is also important to have the longitudinal axis of the die normal to the face. The die illustrated in Fig. 4 may be used safely and will not produce check marks. The die is the result of considerable experimenting and the trial of many designs. In the investigation the angularity of bell *B* and bearing was changed gradually and the design shown was finally decided upon. This die will not produce check marks even when used beyond its normal life. It has been tested thoroughly by using thousands of dies and drawing millions of pounds of copper wire.

Segregation of cuprous oxide in the copper has frequently been held responsible for check marks. Cuprous oxide has never been absolutely uniformly distributed throughout a wire bar and never will be, but if a die of proper design is used in making wire, any variation in distribution of cuprous oxide will not cause trouble; in fact, the author has never found that variation in cuprous oxide distribution had any bearing whatever on the subject. If drawing conditions are not correct, check marks will be produced on any part of the wire regardless of oxide concentration.

Check marks will form a long, gradual helix around the wire, when drawing conditions are poor. This would, of course, take in areas that were originally the four sides of the wire bar.

Experience indicates beyond doubt that check marks are the result of tearing or surface ruptures in the copper during the various drawing operations and are due to absolutely nothing else. When satisfactory wire or check-marked wire may be made at will from the same bar of copper merely by observing the details described, it indicates that the entire trouble is due to drawing equipment, particularly dies, and nothing else.

Trouble from check marks is very serious with wire mills, inasmuch as these defects cause innumerable breaks on wire machines, which result in delays, loss of production and, in fact, at times complete suspension of operations.

CUP AND CONE WIRE

This defect was described briefly by Frank W. Harris[1] in 1928 and by W. E. Remmers[2] in 1929. Suggestions of the author of this paper were the incentive for Mr. Remmers' paper. The present author has studied this type of defect thoroughly. Some of his work was conducted as early as the year 1922.

According to the author's experience, this cuppy wire may be produced in two distinctly different ways. If the angularity of the die is too great and the draft or reduction on the wire is light, cup and cone wire will be produced. Of course, the greater the angularity of the die and the lighter the reduction in drawing, the greater will be the tendency toward cup and cone conditions. Also, if a continuous wire machine is drafted too tightly, cup and cone wire will be produced.

DETECTING CUP AND CONE TENDENCY

A tensile fracture is the quickest and safest means for detecting cup and cone tendency. Other investigators have had this same experience. The exact point at which cup and cone tendency is brought about in copper wire is frequently difficult to locate, inasmuch as the wire may be ruined in one operation and the cup and cone condition may not manifest itself until considerably farther along in the drawing operations. For example, the damage may really be done on one continuous wire machine and cup and cone condition may not be detected until the next drawing stage is reached, or even the second drawing stage.
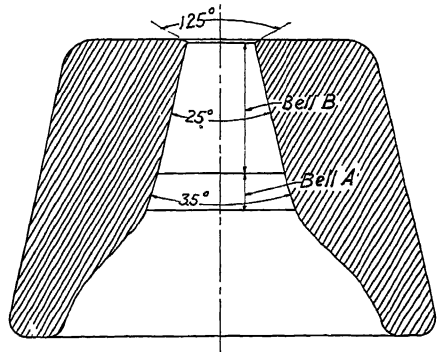
FIG. 12.—DIE WITHOUT BEARING, WHICH PRODUCED CUP AND CONE DEFECTS.

CAUSES OF CUP AND CONE DEFECTS

The cup and cone effect is caused by stretching and breaking of the center of the wire while the outside of the wire is drawn or worked. A $\frac{5}{16}$-in. hot-rolled copper rod was drawn in single block operations one B. & S. number at a time to 0.080 in. dia. through a series of dies similar to that shown in Fig. 12. At the finished size longitudinal sections prepared from the wire showed that cup and cone conditions existed as illustrated in Fig. 13. Tensile fractures made with this wire are shown

[1] F. W. Harris: Distribution of Tensile Strength in Hard-drawn Copper Wire. *Proc. Inst. Metals Div.*, A. I. M. E. (1928).

[2] W. E. Remmers: Causes of Cuppy Wire. See page 107.

in Figs. 2 and 3.   Fig. 13 shows the broken condition in the center of
the wire.

In order to show the importance of a bearing in a die, a piece of the
$\frac{5}{16}$-in. hot-rolled rod was given the same reductions in drawing but was
drawn through a series of dies similar to that in Fig. 14 and cup and cone
conditions did not occur.   Fig. 14 shows the same die as Fig. 12, but
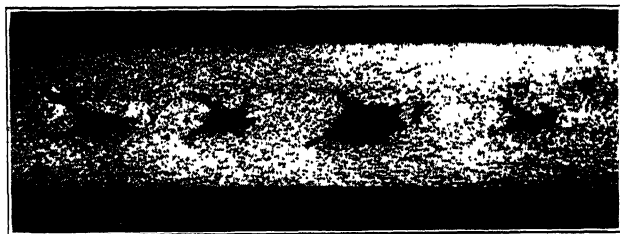
FIG. 13.—CUPPY CENTER OF WIRE DRAWN THROUGH SERIES OF DIES OF PATTERN
SHOWN IN FIG. 12.

there is a 5° bearing in the former and no bearing in the latter.   This
bearing controls details so that the center of the wire is worked but not
stretched, and the cup and cone condition is avoided.

Light reductions taken with dies similar to Fig. 15 did not bring about
cup and cone condition in wire, all of which indicates that a bell of 15°
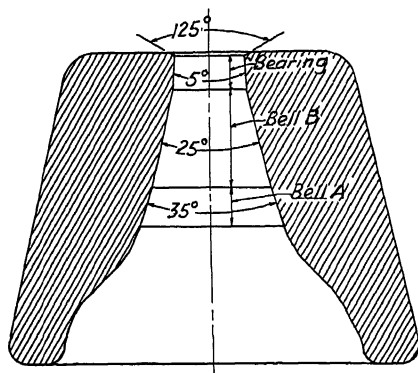
FIG. 14.—DIE SIMILAR TO FIG. 12, BUT
WITH 5° BEARING, WHICH PRODUCED SOUND
WIRE.
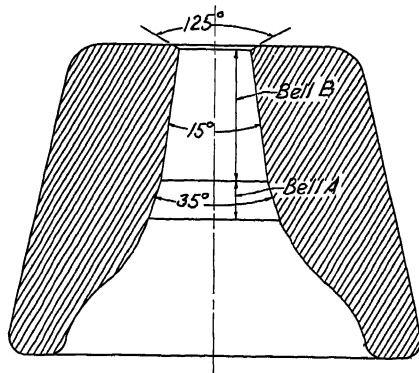
FIG. 15.—DIE WITH 15° BELL, WHICH
PRODUCED   SOUND   WIRE   WITH   LIGHT
REDUCTIONS.

with light reductions will cause the center of the wire to be worked suf-
ficiently to prevent cup and cone condition from occurring.

The difficulty in locating the exact source of trouble and also the lack
of study of this problem has led the wire mills to blame the quality of the
copper for the trouble.   Copper within A. S. T. M. specifications, drawn
through dies according to Fig. 4, on suitable equipment, will be abso-
lutely free from cup and cone tendencies even with the lightest possible

reductions. Cup and cone wire or wire free from these defects may be produced at will from the same bar of copper by simply modifying die design as outlined. This shows that defects are under control and the copper should not be held responsible for the difficulty.

Lack of annealing between the various drawing operations has at times been offered as an explanation of the cup and cone condition in copper wire. Copper is a highly ductile material and if dies are of proper design the omission of annealing operations will not produce cup and cone wire. The author has drawn a 1-in. hot-rolled copper rod to wire as fine as 0.002 in. dia. without any annealing. The wire was hard-drawn all the way and there was absolutely no tendency toward cup and cone condition; in fact, the finished wire was as ductile as wire that has been annealed frequently in the drawing down.
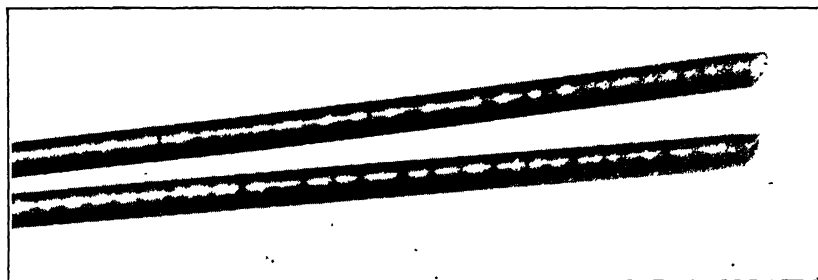
[FIG. 16.—CUPPY WIRE PRODUCED BY DRAFTING WIRE MACHINE TOO TIGHTLY.

It has been mentioned that cup and cone copper wire can be produced by drafting the wire machine too tightly. Fig. 16 shows some wire produced in this way; the chattered condition at the surface of the wire may be observed. This condition is the result of a series of tensile fractures in the center of the wire. The wire has a tendency to be reduced in diameter at these fractures and this causes the chattered appearance. Fig. 17 shows the broken condition in the center of the wire. If the wire is bent or broken in tension, the characteristic cup and cone fractures occur, which are illustrated in Figs. 2 and 3.

If there is not sufficient slip in a continuous wire machine, cup and cone condition may be brought about even with dies of satisfactory design. In other words, cup and cone condition as it occurs in this case has nothing to do with the die design or the quality of the copper. The machine is drafted in such a way that one carrier does not deliver metal to a die as rapidly as the next carrier can remove it, which causes tension in the wire, so that, if the condition is not balanced accurately, the wire breaks. A fine balance can be obtained, however, and a series of internal tensile fractures, as illustrated in Fig. 17, may produce suffi-

cient elongation or stretch to prevent the breaking of the wire on the machine and the drawing continues.

Cup and cone wire and satisfactory wire may be produced at will with the same dies on the same wire machine, using the same bar of copper. Many times the author has demonstrated this. When the wire machine was drafted tightly, cup and cone wire was produced; a rearrangement with the same dies and the same copper produced satisfactory wire. These results were repeated indefinitely.

The production of cup and cone wire as a result of drafting a machine too tightly requires a rather sensitive adjustment, as the wire is almost
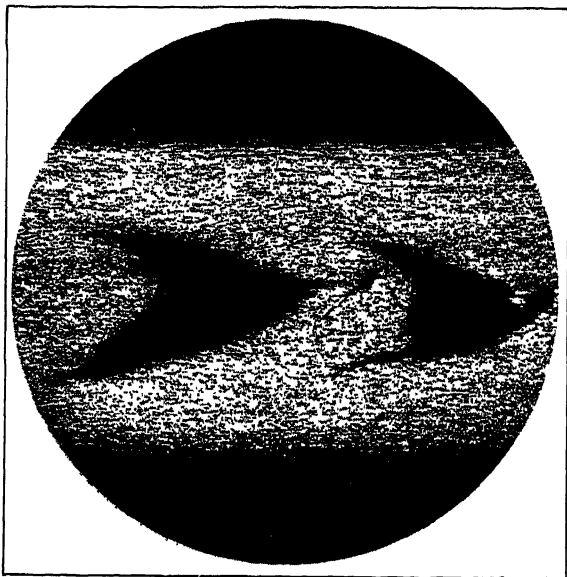
FIG. 17.—BROKEN CENTER OF WIRE SHOWN IN FIG. 16.

broken in tension under these conditions. Cup and cone wire made in this way is usually encountered on continuous drawing machines producing fine wire with diamond dies. The diamond dies, of course, wear very slowly and may gradually bring about suitable conditions for the production of cup and cone wire. Chilled iron dies wear rapidly and there is not much tendency to develop a tightly drafted machine. These dies wear out within a few hours at the most; they are discarded and a new set is placed on the machine. Diamond dies are used for months at a time and if two dies become out of balance, cup and cone wire may result.

This type of defect is extremely elusive and frequently considerable time is required to locate the die that is causing the trouble, as the slightest change unbalances the conditions. Here, again, the quality

of the copper is·invariably held responsible for the defect. A test resorted to many times by the author to prove that quality of the copper is not responsible for the difficulty is to take the dies that are producing cup and cone wire on a continuous machine and draw the wire, one die at a time, on a single block. Invariably the cup and cone condition disappears and perfectly ductile wire is made, indicating that the quality of the copper and the design of the die are correct. The trouble is encountered only when the dies are placed again on the continuous wire machine, which shows that at some point the wire is drafted too tightly. If the machine conditions are poor it is usually easy to detect the exact point at which the cup and cone condition is being brought about. The adjustment is sensitive; there may be difficulty in locating the point of trouble when conditions are becoming just right to produce cup and cone wire and when slight changes in detail will make perfectly ductile wire. This variable action is usually considered conclusive proof by the wire mill that the copper is of questionable quality when, as a matter of fact, the defects are caused by variations in drawing practice.

The author's experience with cup and cone wire indicates that it may be produced by two methods: (1) great angularity of the die and light reductions; (2) dies of proper design when used with improper reductions on a continuous wire machine.

Production of Dies

The importance of die design has been described fully in the foregoing pages. To avoid difficulties, a wire mill should study these details carefully and then standardize on some type of die that will produce copper wire of satisfactory quality. Dies are usually produced by rule of thumb and not by standard methods. The die cutters grind their tools and do not attempt any definite angles, length of bearing, etc. This method of producing dies explains why difficulties occur and disappear at intervals. In order to have all dies of the same design in a mill, it is necessary to work according to some systematic and standardized scheme.

Dies similar to Fig. 4 are simple to make and have been found extremely satisfactory when made of chilled iron, diamonds or tungsten carbide. It is evident that many satisfactory modifications of this design could be obtained. It hardly seems necessary to use a more complicated shape when dies according to this design give everything that is desired.

In order to produce this die in quantities and have every one according to the design, it is necessary to have all tools made to templates, so that the angularity will be the same and one will be interchangeable with another. In Fig. 4, the bearing is supposed to have a length of approximately one-half the diameter of the finished wire. In some cases it has been

found desirable to shorten this bearing slightly, particularly on the larger dies. In order to have the bearing each time one-half the diameter of the finished wire, it is necessary to follow a systematic scheme of cutting.

The first operation in making a chilled iron die is to cut the face with a 125° reamer, as illustrated in Fig. 4. A 15° conical hole is next cut through the die blank, so that the size of the hole at the finishing side of the die will be 92 per cent. of the size the die is intended to draw; for example, if a die of 0.100 in. dia. were to be made, the 15° conical hole would be cut so as to have a size of 0.092 in. at the finishing side of the die. The die is then cut with a 5° reamer until the size is 0.100 in. and the bearing automatically becomes 0.050 in. long or, in other words, one-half the diameter of the wire. The rough part of the die at the entrance is then cut with a 35° reamer and further work on the die is unnecessary. There would, of course, be no objection to extending the 15° bell *B* out to the face of the die, but chilled iron die blanks are not usually cast so as to permit this, which is of course unnecessary. It is very important, however, to have the bell *B* long enough so that the drawing of the wire will start well within it.

Careful inspection of dies before they are placed in the mill is very important. Dies containing blowholes, or other imperfections that will tend to collect foreign material and eventually tear the wire, should either be cut into larger sizes or scrapped. Such dies are likely to give considerable trouble and even one defective die in a lot may cause serious difficulties.

ACKNOWLEDGMENTS

DISCUSSION

C. P. SALMON, Rome, N. Y. (written discussion).—The author should be complimented on diagnosing so clearly the major troubles encountered in wire drawing. Our experiences at the Rome Wire Co. in arriving at the causes of these evils check very well with those expressed by Mr. Jennison. We have found that cuppiness may be produced by: (1) Too great a die angle or (2) the use of good dies in an unusual sequence. One case of the latter had a sequence of reductions as follows: 40—27—36—21—25—20 per cent. The subjecting of the wire first to a heavy draft followed by a lighter one alternating throughout the entire sequence caused cuppiness.

We have found no apparent relation between oxide segregation or content and cuppy wire, as developed by Mr. Remmers.[3] There is a condition that causes unlimited trouble to wire drawers, which they attribute to "poor copper"; what this is actually due to, we are not as yet prepared to say, though it may be related to oxide content. Segregation of oxide from the set surface of wire bars is often a cause of brittle edges in flat rolling.

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[3] See page 107.

One important factor in die design which Mr. Jennison has not discussed is drawing speed. Will cuppiness occur with dies of improper angle if wire is drawn at low speeds? If not, is there a relation between the angle and length of land for different speeds? In other words, would dies now considered satisfactory still be satisfactory at higher speeds?

J. W. SCOTT, Chicago, Ill.—The second paragraph on page 121 of Mr. Jennison's paper would lead us to believe that tough-pitch copper is a uniform product. My experience in casting heats of tough-pitch copper would lead me to believe that this is not necessarily the case. I think it is a fact that bars cast from the same heat of copper are likely to vary one from another. Also, two heats from the same refinery are likely to vary one from another; and further, a wire bar itself is not a uniform product throughout.

Mr. Jennison does not so state, but he may have been in a position to use copper that was of more uniform composition than the limits established by the A. S. T. M. specifications. However, in most work we must assume that the commercial copper varies within the limits of the A. S. T. M. specifications, and as such is not an entirely uniform product.

H. BLOUNT, Chicago, Ill.—Mr. Jennison's paper is of interest to all those connected with the drawing of copper wire, more particularly as all probably have experienced at some time this trouble of cuppy wire. I do not think it is all the product of the wire mill. We feel that copper is largely responsible for this trouble. Our experiments so far have substantiated not only Mr. Jennison's experiments but also those of the Rome Wire Co., that cuppy wire can be produced at will by irregularity of die reductions, more particularly if light reductions are followed by a heavy reduction. As an example of that, if, in drawing rod, we start with a $14\frac{1}{2}$ per cent. reduction, followed by a 25 per cent. reduction, followed by a 16 per cent. reduction and then come back again with a 25 per cent. reduction, we will invariably get cuppy wire.

So far as the wide angle is concerned, our experiments do not substantiate this; sometimes we have produced cuppy wire with a wide angle; at other times, we have not. Our standard method of drawing No. 12 wire is through several reductions, with a die design practically the same as that illustrated in Fig. 4. We will not produce cuppy wire with the same number of reductions if we use wide-angle dies. Neither will we produce cuppy wire all the time if we reduce the drafts and put the full complement of dies to the capacity of our machines of 10 dies. Sometimes we will produce cuppy wire; usually we will not do so even with the wide angle of dies. Therefore, we do not believe that all the blame rests with the dies.

Mr. Jennison also says, on page 131 that this phenomenon will not exist if single die reductions are used. We have drawn wire by single die reductions and from one coil of copper rod we produce cuppy wire, using dies of standard shapes as shown by Fig. 4. With the same dies and another coil of rod, we will not get cuppy wire. The only condition changed is the coils of copper rod. In answer to Mr. Salmon, I might say that these experiments were carried on at a speed of about 250 ft. per minute. Therefore, we feel that copper is largely and more responsible than the shapes of the dies or the condition of the machines.

H. P. ARKEMA, Chicago, Ill.—Mr. Jennison mentions that the two defects, check marks and cup and cone breaks, are produced by dies as shown in Fig. 10 and 12, respectively. The designs of the dies shown in these figures are practically the same, with the exception of the angle of bell B. The die which produced cup and cone break has a 25° angle as compared to the 30° angle of the die that produced check marks.

On several occasions we have found that with dies of the design shown on Fig. 14, and all other wire-drawing conditions constant—that is, wire-drawing speeds, wraps on capstans and compound—wire with check marks and wire with cup and cone breaks was produced. In trying to determine the cause, we found that the copper used in making the wire with check marks was low in oxygen and had a tendency towards brittleness and the copper that produced the cup and cone breaks was relatively high in oxygen. The oxygen content of the copper producing check marks was below 0.030 per cent. and that producing cup and cone breaks was above 0.06 per cent.

W. E. REMMERS, Chicago, Ill.—My conclusions are printed on page 115.

Mr. Jennison referred only to the defects caused by the angularity of the die and the tight drafting of the wire-drawing machine. These were the suggestions that were the incentives of the previous investigation, which led us to the conclusion that oxygen content of the copper had to be considered as a very effective factor in producing cuppiness.

FIG. 18 —WIRE BAR THAT BROKE ALMOST ENTIRELY ACROSS.
FIG. 19.—SMALL BREAKS ALONG LOWER SECTION OF WIRE BAR.

In tightly drafting a wire-drawing machine by wiping the capstan free from grease and drawing wire, we found that instead of producing a cup and cone break, the wire broke after drawing rather short lengths. This break was distinctly a brittle break, probably due to a burning of the wire on the capstan.

At the bottom of page 128, in Mr. Jennison's paper, the following appears: "Copper within A. S. T. M. specifications drawn through dies according to Fig. 4, on suitable equipment, will be absolutely free from cup and cone tendencies even with the lightest possible reductions." This seems a bit positive. Table 1 shows six analyses taken from random samples of cuppy wire, all of which conform to the A. S. T. M. specifications.

TABLE 1.—*Analyses of Cuppy Wire*

Sample No.	Copper, Per Cent.	Lead, Per Cent.	Arsenic, Per Cent.	Silver, Per Cent.	Sulfur, Per Cent.	Oxygen Per Cent.
1	99.92	0 003	<0 001	<0.003	0 002	0 071
2	99.91	0.002	<0 001	<0.003	0.002	0.083
3	99.93	0.003	<0.001	<0 003	0.001	0.063
4	99.92	0 003	<0.001	<0 003	0 002	0 073
5	99.92	0 002	<0.001	<0 003	0 002	0 063
6	99.91	0 002	<0 001	<0 003	0 002	0 078

The copper varies from 99.91 to 99.93, the lead is 0.003 or under, arsenic less than 0.001, silver under 0.003, while the oxygen varies from 0.063 to 0.083 per cent. I do not believe any of us would accept any of these as being desirable oxygen contents for the satisfactory drawing of wire.

I have a few illustrations which are more or less in agreement with Mr. Scott's discussion.

Mr. Jennison's statement in the second paragraph on page 121 has been discussed. Fig. 18 is a piece of wire bar after one of the earlier passes in the rolling mill where the wire bar broke almost entirely across the section.
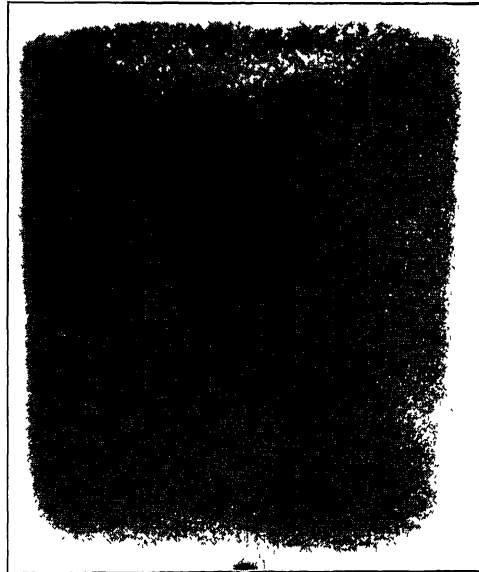
FIG. 20.—CROSS-SECTION WAFER FROM CENTER OF BAR.

Fig. 19 is of a wire bar similar to that in Fig. 18, containing a number of small breaks along the lower section of the bar. The nonuniformities of wire bar have been discussed. These two specimens were heated with other bars that rolled satisfactorily.

Fig. 20 shows a radiograph of a wafer approximately ¾ in. thick cut in cross-section from the center of a wire bar. Mr. Jennison says that the bars have been cast sound. This figure shows the copper in a highly porous condition. The gassy condition in

this bar, which incidentally was picked out of the regular run of copper bars received in a carload shipment, shows the highly spongy condition on the top which exists down some ¾ in., and a slightly gassy condition which extends to the entire depth of the bar.

Fig. 21 is a photomicrograph of a section lower in the bar, showing the numerous gas pockets.

Fig. 22 is a radiograph of a section of wire bar, showing some segregation. A dark line follows the general outline of the mold. Much fainter and slightly lower in the bar is another one. These dark lines indicate a segregation of some material with a greater atomic weight than copper. What it is, I will not attempt to describe—it may be lead, gold, or silver, or something of such nature—but there is evidently a segregation of some material that is less penetrable by X-rays.

Fig. 23 is a photomicrograph of a piece of wire bar showing excessive oxygen content. Again one would hesitate to say that this represents good copper for wire drawing. This sample was also taken from the regular run of wire bars as received.

Fig. 24 is a cross-section of a piece of wire rod. It is apparent that a distinct metallurgical break exists down through the center of the rod. Perhaps it is a result
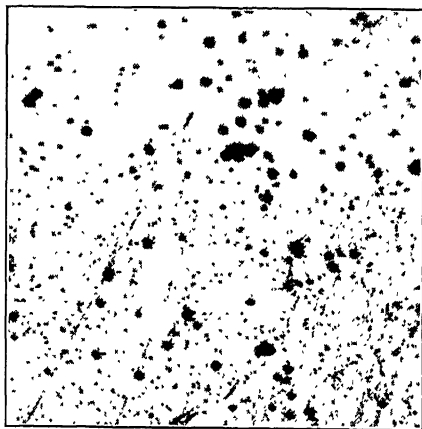
FIG. 21 —SECTION LOWER IN BAR SHOWN IN FIG. 20, CONTAINING GAS POCKETS.
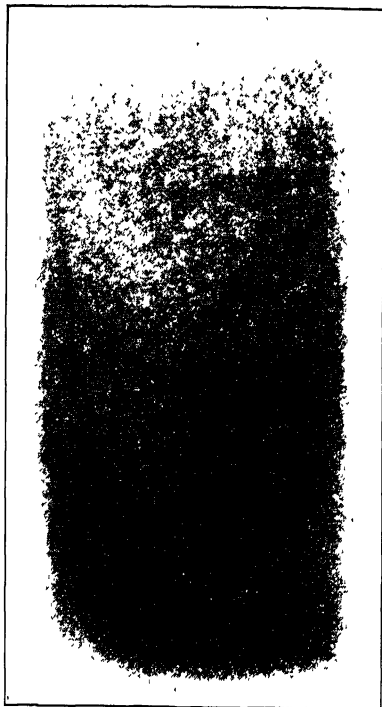
FIG. 22.—SEGREGATION IN WIRE BAR.

of the spongy condition at the top of the wire bar. Nevertheless it assists in illustrating that copper wire bar is not all sound and uniform.

Over a period of two years, when using the same design of dies, the same speeds and a uniform drawing practice, the average of each year separately showed a marked difference in the amount of cuppy wire produced. During the first year cuppy wire was produced at various times in the mill for a period of six weeks, and at no other time in the year. The second year cuppy wire appeared in almost a negligible amount, not more than a few hours at a time during which cuppy wire could be found in the mill. Because of the discrepancy in averages taken over so long a period of time, it seems reasonable to conclude that the quality of wire bar is a factor to be considered when wire defects are studied.

S. McMULLAN, Chicago, Ill.—Mr. Jennison's die design, Fig. 4, is the design of die that we have used in our mill for the past five years. About the end of 1923 we standardized on this die design, made up blueprints of it, laid out the tools and methods of manufacturing it, and all the necessary gages for the die department to keep the dies according to specification.

Nevertheless, this die is not a cure-all for the troubles in the wire mill. We have time and time again run into cuppy wire using this die. As far as we know, the compound, the wire-drawing machines, and the die which we believe is about the best design we can get, did not keep us out of this trouble. Sometimes we get check-marked wire, which is brittle and breaks, with the same die. At other times we get cuppy wire with that die.

In order to make sure that the dies were absolutely according to standard, we have had high-grade diamond-die makers polish and lap these dies. We have had the very best toolmakers that we could find in our organization make these dies and lap them
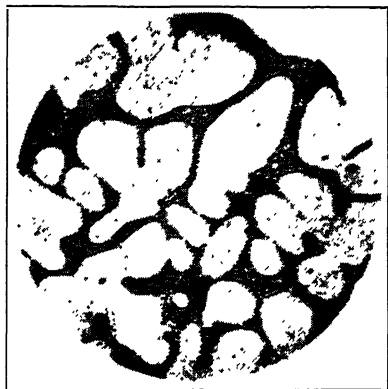
FIG. 23.—WIRE BAR WITH EXCESSIVE OXYGEN CONTENT.
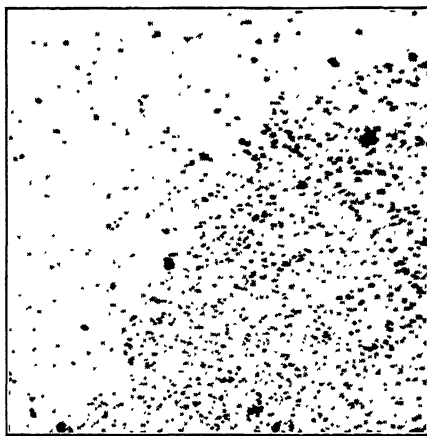
FIG. 24.—METALLURGICAL BREAK DOWN CENTER OF WIRE ROD.

according to our standards, and when the dies were completed we would insert plugs in them, take the plugs out, project them with a projector, and measure them up with the standard, and we would find they were as nearly correct as could possibly be expected.

But these high-grade dies made by diamond-die makers, although they were made from chilled iron and made by highly paid toolmakers, would not stop the production of cuppy wire when we were in a run of cuppy wire. Consequently, we must look to some other source than dies as the only answer to cuppy, brittle, or check-marked wire in wire drawing.

Our study of the die situation goes back to probably 1919–1920. We are using chilled iron dies of the type described in this paper as the proper die at the rate of about 1,000,000 a year. We have had made millions of pounds of wire through them, and we have troubles with cuppy wire at intervals, although we know of no other changes in the mill. We have come to the opinion, after gathering considerable data—and these data indicate that our opinion is founded fairly well on facts—that keeping the die and all other conditions constant, we have, as has already been remarked, obtained brittle wire, check-marked wire when the oxygen ran too low in

high-set bars. When the oxygen ran too high we got cuppy wire. When the oxygen runs about average—and by average I would say about 0.04 or 0.05—the copper running at 99.94 and 99.95, we have found it very difficult to produce cuppy wire under such conditions.

J. T. KEMP, Waterbury, Conn.—Mr. Jennison has handled wire bar from all the commercial refineries of the Atlantic seaboard day in and day out for years. In the course of his work he must have run across bars that would give a bad shadowgraph, bars that were too high or too low in oxygen, according to the remarks that have just been made, and yet he has made the statement that commercial wire bars meeting the A. S. T. M. specifications, properly handled, through proper dies, will make good wire. I think his statement stands.

As to the effect of high speeds and low speeds, I am unaware of any appreciable difference in effect that results from variations in speed within a normal commercial wire-drawing practice.

The photographs that Mr. Remmers has shown us of cracked wire bars, partly rolled, are interesting. Everyone who is concerned with rolling copper wire bars and drawing wire has seen bars cracked exactly like them. It cannot always be charged to the quality of the copper, and I say that, too, from the point of view of a copper-wire manufacturer. It is not impossible to gas a wire bar in heating it and cause exactly those fractures to occur in rolling.

One or two of the speakers have referred to the occasional occurrence of cuppy wire in the course of normal practice with no great changes, or acknowledged changes in the die design or practice. It is, of course, very difficult to discuss points like that at short notice and long range, but in view of the fact that cuppy wire can be produced by variations in the tightness of drafting on continuous wire machines, I would suggest that the next time this occurs they look to the conditions of their carriers and see that the latter are in series of proper proportions, diameter to diameter as compared with the diameters of the dies. As Mr. Jennison has said, slight variations in the diameter of the die due to wear, particularly of diamond dies, are likely to bring about the delicate state where the wire almost breaks but does not quite do so. Then cup and cone fracture occurs. If the carrier heads run much too fast the wire will break; if they run just a little too fast, cup and cone fracture will occur. If they run just right, the wire becomes perfect.

W. H. BASSETT, Waterbury, Conn.—I was familiar with Mr. Jennison's work at the time it was going on and I know something of the great amount of experience upon which it was based. I think that Mr. Jennison's statement that wire bars meeting the A. S. T. M. specifications, if properly handled in drawing, will not give cuppy wire, is absolutely correct. I have had a great deal of experience in that particular line. No one would claim that wire bars that were cracked in rolling would make good wire on further drawing. The cracking of wire bars is a matter which we think is entirely independent of the purity of the copper.

The causes for the cracking of wire bars have been under discussion but I do not know that anybody is yet ready to say the last word. The principal cause probably, is the manner in which the wire bar is held in the mold during the period of solidification. When the copper is partly solidified, if it is held in the mold so that it cannot slip, something has to happen, and the wire bar is cracked. Those cracks usually are along the bottom edge of the bath.

One of the tricks that is sometimes used to reveal the cracks is to pour kerosene oil over the bar, wipe it as dry as possible and then rub chalk along the corners. The kerosene will exude from the very fine cracks, which ordinarily would hardly be noticed, and show where it was cracked.

If guide scratches or fins occur in rolling and these are rolled in, it is impossible to make good wire from the rod. It is not fair to bring such things into the discussion of the paper, which is based upon wire bars being normally handled in rolling.

The work which Mr. Jennison did in the mill covering a number of years of experience preceding this final work to prepare the paper, was also reenforced by a wide experience in mills having trouble in drawing wire. Mr. Jennison has been to a number of mills to observe the different methods of making wire from wire rods, and finally went to a number of mills in Europe where difficulties were being met. This paper is his answer to all the difficulties in wire drawing which he has encountered.

It is my contention, after long experience, that given copper meeting the A. S. T. M. Standard Specifications, given dies of proper design, and properly drafted machines, copper can be drawn indefinitely. In other words, one can start with as large a bar as the mill will roll and draw it as fine as the machines will draw it, and the result will be wire which is perfect in every respect.

H. C. JENNISON (written discussion).—It has been the author's experience that drawing speeds have no effect upon the defects described in this paper.

Copper wire bars that have cracked in hot rolling, wire bars that possibly crack even before hot rolling and wire bars containing various types of defects have been mentioned in this discussion. This is an entirely different subject and has no bearing on the present paper. Defective wire bars do not produce check marks in copper wire, neither do they produce cuppy wire.

The American Brass Co. handles from time to time all brands of high-conductivity wire bars. The author has been intimately connected with the production of copper wire for many years. The American Brass Co. positively does not encounter check marks and cup and cone wire in its wire mills. All copper received is within A. S. T. M. specifications and if dies are of proper design and the wire machines are suitably drafted, any wire mill can draw such copper into wire free from check marks and cup and cone defects. Slip on a continuous wire machine is a very important detail; frequently wire mills do not provide a sufficient amount of slip, and cup and cone wire results. At times it is very difficult to locate the exact point at which cup and cone wire is being produced, particularly when the tension in the wire machine is just sufficient to bring about these conditions. Frequently a very sensitive adjustment is obtained and cup and cone wire may be produced for a few minutes and then perfectly ductile wire be drawn for a short period. This is usually taken as conclusive proof on the part of the wire mill that the copper is of variable quality, but is not the case; the results are due to variations in conditions on the wire machine and the quality of the copper is not in any way responsible.

A number of those taking part in this discussion still appear to be of the opinion, in spite of the details outlined in the paper, that the copper is responsible at times for checks marks and cup and cone defects occurring in the wire, although the copper may be within the A. S. T. M. specifications. The author would be pleased to have submitted to him for drawing into ductile wire any copper that is within the A. S. T. M. specifications and which, in their opinion, cannot be drawn into wire free from check marks and cup and cone defect.

Correlation of the Ultimate Structure of Hard-drawn Copper Wire with the Electrical Conductivity

By R. W. Drier* and C. T. Eddy,† Houghton, Mich.

The conductivity of copper wire is of prime importance to the electrical industry and consequently to the copper refiner and wire manufacturer. Annealed copper wire has a higher conductivity than hard-drawn wire, but, on the other hand, its tensile strength is lower.

In an attempt to explain the reasons for these changes in property. or at least to study the conditions existing in these two types of copper wire, the experiments described here were carried on in the Department of Metallurgy of the Michigan College of Mining and Technology

This is only a partial and preliminary report on some of the work done to date on a research program of which the object is an intensive study of copper. It is offered with the hope that, though it is not an exposition of the most rigorous of conclusions, the general trend of inferences which may be drawn will be of value and interest.

Effect of Direction of Drawing

In 1928 some work was done on hard-drawn copper wires to determine whether wire drawn in a continuous machine (that is, all in one direction) would have a different structure from wire that had a reversal in direction at some stage of the drawing process.

The diffraction spectra obtained indicated that as the position of the wire rayed approached the core, a preferential crystal orientation existed, and that the closer to the core the more preferred was the orientation. The data obtained partly corroborated the work done by Schmidt and Wasserman[1] and by Clark.[2]

Samples Used in Following Investigation

The samples selected for use in both the diffraction work and the resistivity measurements were taken from Nos. 6, 8, 10 and 12 gage

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† Department of Physical Metallurgy, Michigan College of Mining and Technology.

[1] *Ztsch. f. Metallk.* (August, 1927) 325.

Ztsch. f. Phys., **24**, 779.

[2] *Heat Treating and Forging* (1928) 257.

(B. & S.) commercial wire, both hard-drawn and annealed. The wire was produced from standard 220-lb. wire bars, hot-rolled to $\frac{1}{4}$ in. and hard-drawn in one direction to size. In addition, observations were made on 10-gage wire. which was drawn from a piece of native copper without melting. The annealed wires used were subjected to a temperature of 820° F. for 1 hr. and 15 minutes.

Table 1 gives data relative to the composition and conductivity of the wires discussed in this paper.

TABLE 1.—*Composition and Conductivities of Wires Discussed*

Wire	Metal Content, Cu + Ag	As	Conductivity, Per Cent.
No. 12, hard-drawn.	99.94	0.000378	97.7
No. 6, hard-drawn........................	99.94	0.000378	97.8
No. 6, annealed..........................	99.93	0.000370	99 8
No. 10, hard-drawn from native copper......	99.96	0.000310	99.8
No. 10, same as No. 10, but annealed.......	99.96	0.000310	102.5

In order to study the changes in ultimate structure from the surface to the core of the wire and to observe any changes in conductivity which may accompany these structural changes, observations were made on wires whose outer layers were removed in successive stages by dissolution in 25 per cent. nitric acid. The etching was carried on in such a manner that the diameters of the wires were reduced in stages of approximately 0.5 mm. Various methods of etching were tried, all of which yielded identical results. The method that was adopted consisted in placing the wires in a nearly vertical position in a cylinder and causing them to rotate by mechanically agitating the solution. For each stage, after one-half of the etching was accomplished, the wire was turned end for end in the solution and the etching completed. It was generally observed that as the hard-drawn wires etched the cross-section gradually became elliptical. The difference between the lengths of the major and minor axes of the cross-section at the core was found to be as great as 50 per cent. In the annealed wires this elliptical etching was not observed and the cross-section remained practically circular to the core.

The diffraction patterns were obtained from samples that were taken immediately adjacent to those used for the resistivity measurements. In addition, diffraction patterns were taken of the original wires (those used for the resistivity measurements) before etching and after the last etching had been made and the resistivity determined. These latter patterns agreed precisely with the first and last patterns of the series made from a single wire and illustrated in Fig. 2.

MICROSCOPY

A microscopic study of the wires was made but no difference in structure was observed between the material at the surface and that near the core. The ends of the wires were etched to approximately 0.5 mm. dia. in order to observe the relative directions of the minor and major axes of the elliptical cross-sections which seemed to persist in the hard-drawn wires. Longitudinal sections were then made relative to these axes and the microstructure was studied. No structural differences were observed in these sections and all revealed uniform elongated grains
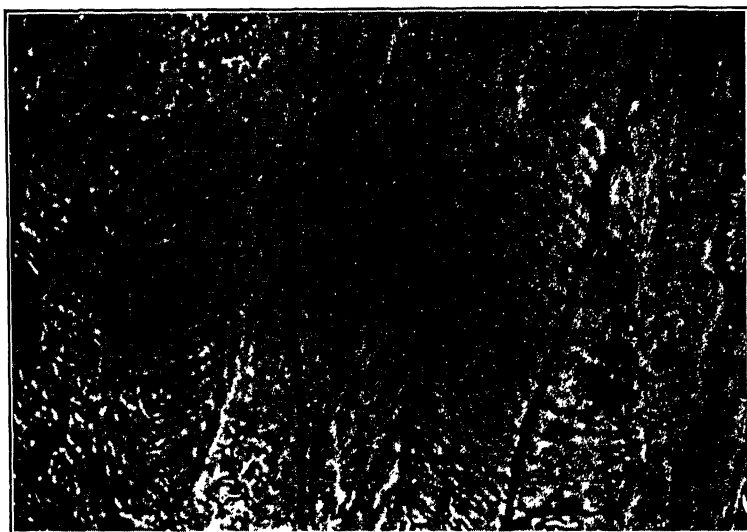
FIG. 1.—HARD-DRAWN COPPER WIRE SHOWING NORMAL HARD-DRAWN STRUCTURE, HIGHLY ELONGATED GRAINS AND MANY SLIP PLANES. × 3500.

similarly oriented and presenting the ordinary slip structure of hard-drawn copper. The transverse sections were also investigated and showed no essential difference throughout. This work corroborates that of Harris.[3]

Fig. 1 is a photomicrograph of the No. 6 hard-drawn wire showing the ordinary elongated grains and slip structure.

DIFFRACTION

The diffraction work was done on a General Electric unit, late model, using a molybdenum water-cooled target Coolidge tube, operating at 20 ma. and 30,000 volts. The familiar Hull cassette with zirconium dioxide

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[3] F. W. Harris: Distribution of Tensile Strength in Hard-drawn Copper Wire. *Proc.* Inst. Metals Div., A. I. M. E. (1928) 518.

filters as an integral part of the cassette was used. The filters permit transmittance of radiation which approximates the monochromatic.

The sample in wire form was placed in the cassette in the slot meant to support a capillary tube of an unknown. The wire was adjusted in the slot so that its top surface was bathed by the central beam. Diffraction patterns were obtained of the several sizes of wires mentioned. Spectra were obtained of each wire in its separate stages of etching. The patterns of the different wires were so similar that it was felt that a single series would be representative of them all. Fig. 2 shows the diffraction patterns of the No. 6 B. & S. hard-drawn copper wire in its several stages of reduction from 4.12 to 0.09 mm. dia. Figs. 3a, b, c show the spectra of No. 6 B. & S. annealed copper wire at the surface and at the core. The similarity between the two is indicative of the structural similarity which might be expected of wire so treated.

As Fig. 2 shows, the preferred orientation first became noticeable when the wire was etched to a diameter of 2.96 mm. and became more pronounced as the core was approached. If in the pattern of the surface or skin of the wire the line intensity for the 110 planes is arbitrarily taken as 10, the following relative intensity changes occur:

The 111 planes decrease from 10 to 0.

The 200 planes do not vary perceptibly.

The 220 planes practically double their intensity.

The 311 planes decrease from 8 to 3.

The second order of 111 planes practically disappears.

The second order of 100 planes do not vary.

The third order of 111 planes disappears.

It is fairly easily deduced from the preceding data that the orientation is one in which a cube edge is parallel to or in the fiber axis and normal to the X-ray beam.

As mentioned, the wires became somewhat elliptical in cross-section as they approached their cores. Peculiarly, the patterns taken with the X-ray beam parallel to the major diameter of the ellipse differs from perpendicular to the major diameter. When the beam is parallel to the minor diameter the spectral line representing the 111 planes becomes slightly visible again (Fig. 3d).

With the exception of the reappearance of the 111 lines, the evidence is all in favor of an orientation that would permit the 110 planes to be parallel to and rotate along the plane of the X-ray beam. The cube edge being parallel to the direction of drawing, that is, the fiber axis, would be one such orientation. This would permit maximum reflection (on a Hull pattern) from the 110 planes and a minimum from the 111 planes. The authors are of the opinion that such is the preferred orientation as the core is approached.
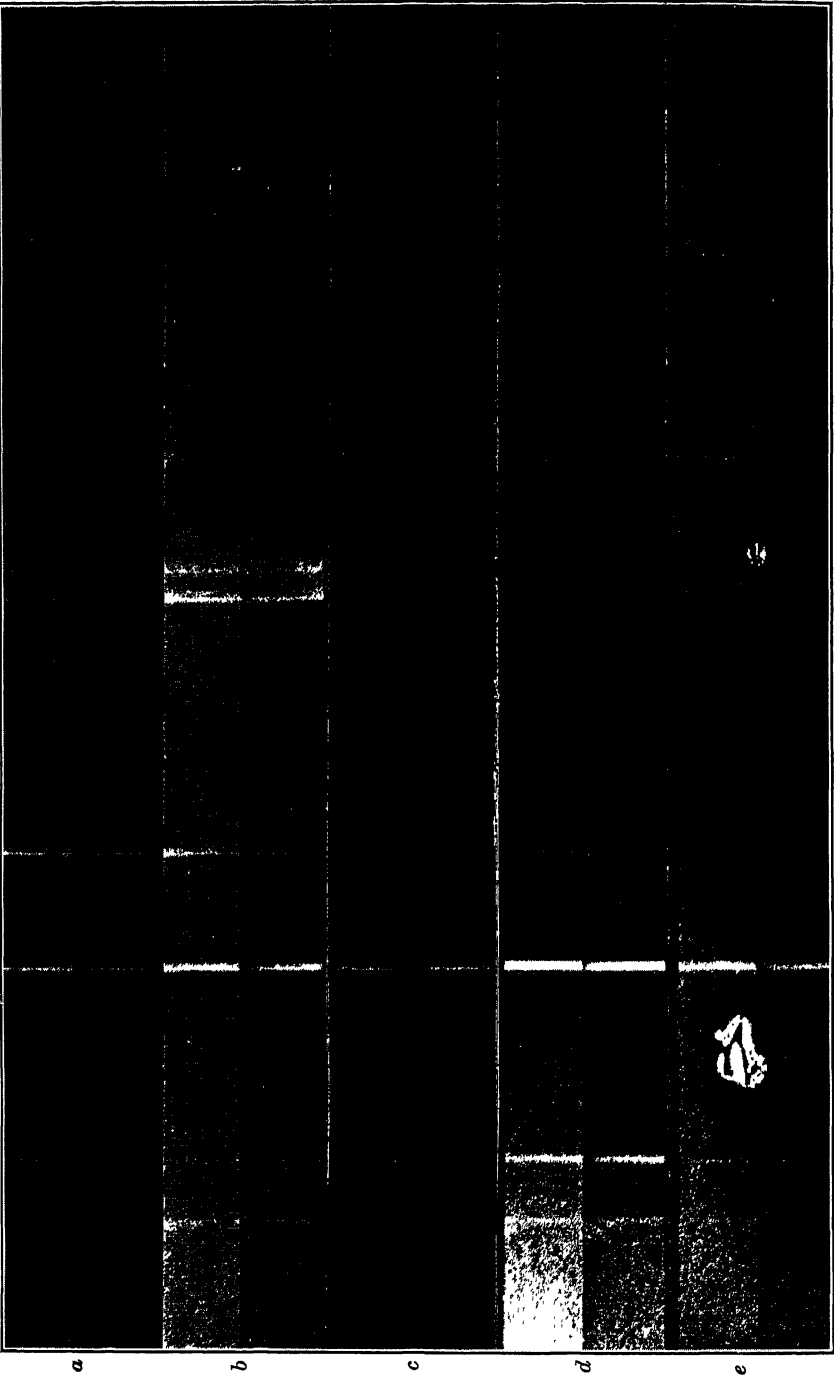
FIG. 2 *a-e.*
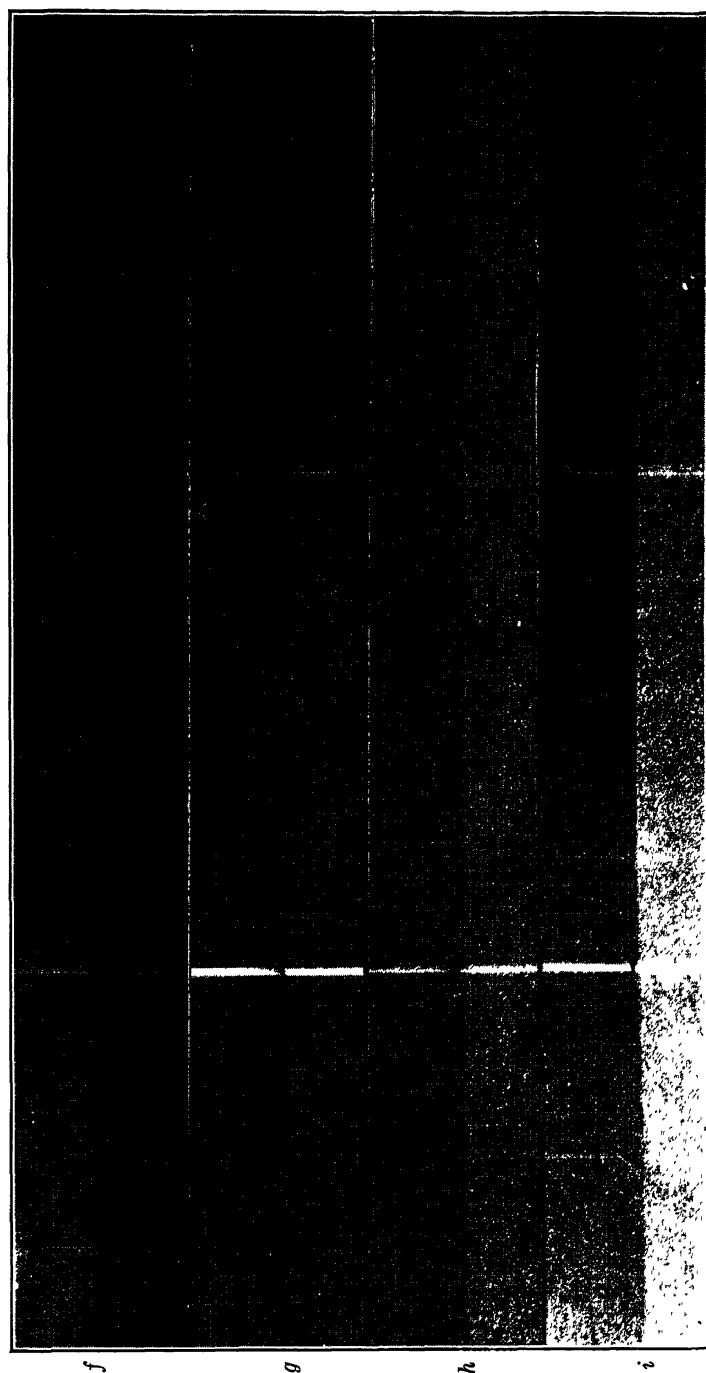
FIG. 2.—No. 6 B. & S. COLD-DRAWN COPPER WIRE IN THE SUCCESSIVE STAGES OF ETCHING.
Diameter of Wire after Etching and before Raying

a. 4.115 mm.
b. 3.5 mm.

c. 2.96 mm.
d. 2.35 mm.

e. 1.95 mm.
f. 1.15 mm.

g. 0.45 mm.
h. 0.25 mm.

i. 0.13 mm.
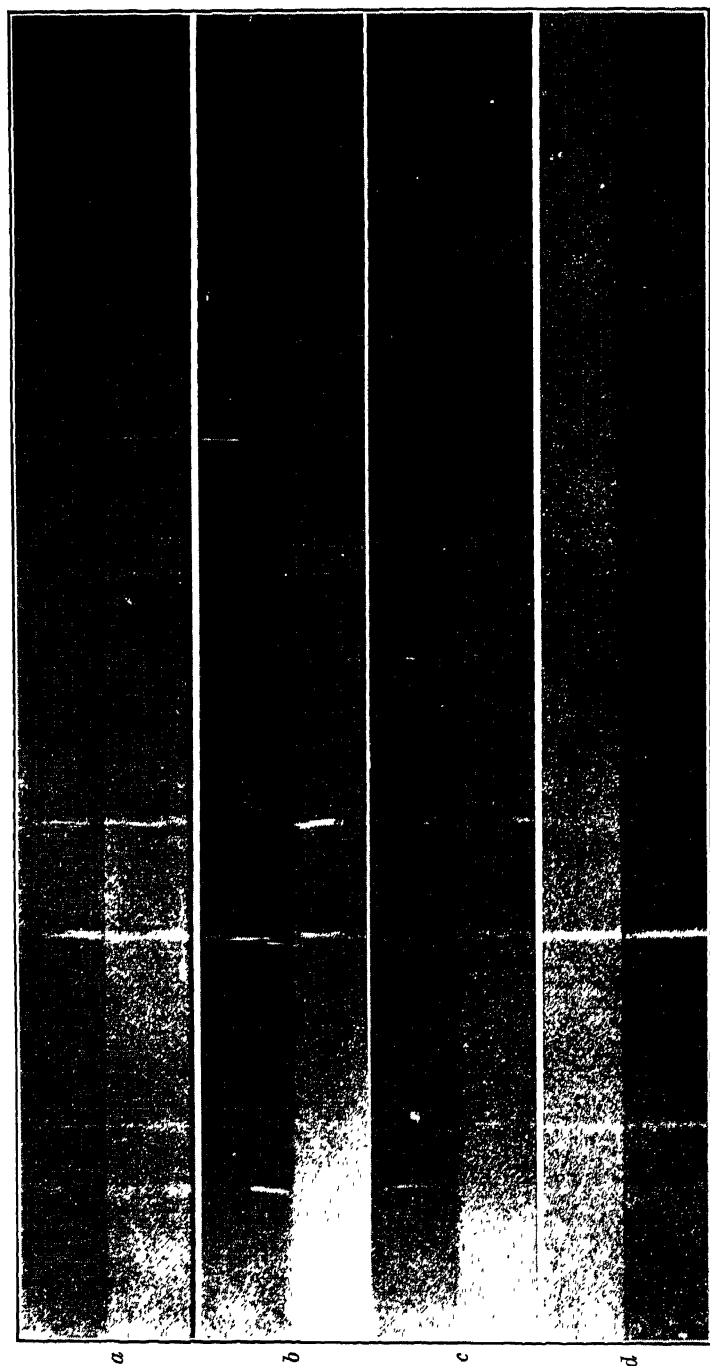
FIG. 3.—*a.* No. 6 B. & S. ANNEALED COPPER WIRE.   *b.* No. 6 B. & S. ANNEALED COPPER WIRE, ETCHED TO −0.5 MM. DIAMETER. *c.* SAME AS No. 2, ROTATED 90°.   *d.* No. 6 B. & S. HARD-DRAWN COPPER WIRE, ETCHED, AND RAYED PARALLEL TO THE MINOR AXIS OF THE CROSS-SECTION.

Schmidt and Wasserman[4] state that the core of hard-drawn copper wire will have representatives of both orientations; that is, some unit cells with the cube edge parallel to the fiber axis and some cells with the body diagonal parallel to the same. If the body diagonal were parallel to the direction of drawing, the 111 planes would be indicated, but with a face-centered cubic material it is not clear why this should occur only when the wire is in the position mentioned above. No explanation is offered, none being felt necessary in this paper, but this phenomenon is mentioned merely for its peculiar interest in connection with the subject of unit cell orientation.

RESISTIVITY MEASUREMENTS

For the determination of the changes in specific resistivity throughout the sections of the wires, measurements were made on the original wires before etching and on the wires after each successive etching.
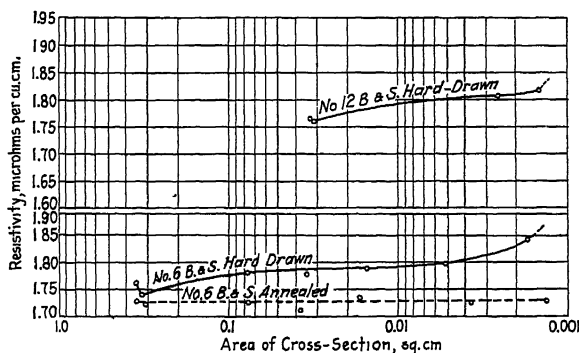
FIG. 4.—CURVES CORRELATING RESISTIVITY CHANGES WITH CHANGES IN CROSS-SECTIONAL AREA OF THE WIRE.

The potentiometric method was used and direct e.m.f. readings made to 10^{-6} volts. The wires were placed in a special bridge and mercury end contacts were used in order to insure parallel lines of flow (especially for the heavier wires). A definite current, accurately measured, was passed through the wires and the drop in potential between two intermediate knife-edge contacts was measured on the potentiometer. The Leeds & Northup type K potentiometer was used for this purpose. The distance between the knife-edges was accurately adjusted and maintained constant for all observations.

For the original wires the areas of cross-sections were determined after measuring the density by weighing the wires in water and air. The area was then calculated from the volume thus determined and the length of the wire. These areas were checked by measuring the diam-

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[4] Schmidt and Wasserman: *Op. cit.*

eters with a micrometer caliper as well as with a micrometer microscope under a magnification of 70 dia. The areas of cross-sections thus determined were found to agree within the necessary limits of accuracy. For the intermediate samples, where there was a likelihood of differential etching along the length of the wires, the micrometer measurements were carefully checked. As an added precaution, after making the last potentiometric measurement, the wire was cut under the knife-edges and the cross-sectional area of the part of the wire actually measured was again determined by all three methods mentioned above and found to agree.

In Table 2 the results of these measurements are tabulated for the wires chosen as being representative. Fig. 4 is a graphic representation

TABLE 2.—*Change in Specific Resistivity with Cross-sectional Area*

Wire B & S Gage	Area at Section, Sq Cm.	Specific Resistivity, Microhms per Cu Cm.
No. 12, hard-drawn...........................	0.0333	1.764
	0.0314	1.762
	0.00255	1.808
	0.00149	1.819
	0.00129	1.914 Max.
No. 6, hard-drawn..................	0.1350	1.762
	0.1323	1.738
	0.0782	1.781
	0.0349	1.775
	0.0151	1.789
	0.0052	1 797
	0.00172	1.841
No. 6, annealed................................	0.1350	1.728
	0.1320	1.721
	0.0775	1.726
	0.0378	1.712
	0.0172	1.736
	0.00371	1.727
	0.00134	1.729
No. 10. hard-drawn from native copper............	0.0557	1.729
	0.0529	1.698
	0.0137	1.745
	0.00288	1.793
	0.00135	1.840
No. 10, same as No. 10, but annealed............ .	0.0555	1.683
	0.0132	1 628
	0.00295	1.682
	0.00141	1.725

of these results plotted logarithmically so as to more nearly represent the cumulative nature of the changes in the resistivity observed.

No explanation of these curves seems necessary. As was previously generally accepted, the resistivity in the skin in hard-drawn wires was found to be higher than that in the wires after the first etching. More correctly stated, the average resistivities of the original wires were higher than the average resistivities of the wires after the outer surfaces had been dissolved off. However, for the hard-drawn wires the curves representing these averages resistivities abruptly changed in slope after the first etching, and upon subsequent etchings were found to rise to a maximum value as the longitudinal axes of the wires were approached. For finer wires, where it was thought that the small current flow may have some heating effect, thus increasing the resistivity, the probable rise in temperature occurring in the wire (assuming no radiation) was calculated for the time necessary to make an observation. It was found that the increase in temperature would be negligible for the currents used. To check the specific resistivity in these finer wires various current strengths were used and the drop in potential in the wires was determined for each. The results shown in the curves were obtained by using currents sufficiently low in strength to allow the heating effect manifested to be negligible.

CONCLUSIONS

Crystal orientation in hard-drawn copper wire becomes preferred as one penetrates from the skin to the core.

The orientation is one in which the cube edge is parallel to the fiber axis or direction of drawing.

The resistivity measurements indicate that the resistivity increases with the degree of this particular type of preferred orientation.

From this work and that of Harris it also appears that a similar relation exists between the tensile strength and the degree of preferred orientation.

Crystal orientation in annealed copper wire is not preferred.

The average specific resistivities from the skin to the core in annealed copper wires did not vary. In the event that the resistivity varies with the degree of preferred orientation, this is as would be expected.

The nature of the material at the core of the hard-drawn wire, owing to its preferential orientation, approaches that of a single crystal. Hence, evidence seems to refute the theory of higher conductivity in single crystals.

DISCUSSION

W. H. BASSETT, Waterbury, Conn.—We have studied this subject from the metallographic standpoint and know, of course, that when wire is drawn crystals become oriented very strongly in one direction. We have, however, made no X-ray examinations of crystals in hard-drawn copper wire.

W. B. PRICE, Waterbury, Conn.—In my discussion of Mr. Harris' paper[5] I brought out the fact that the difference in physical properties between the skin and the center of the core on hard-drawn wire was probably due to self-annealing of the wire, and Mr. Bassett concurred in my opinion. I think that has a decided bearing on the question of the disappearance of the 111 planes of the first, second and third order.

J. W. SCOTT, Chicago, Ill.—In Table 1, the authors show an electrical conductivity of 102.5 per cent. after annealing No. 10 gage wire. That is a rather high conductivity for normal copper. The explanation may lie in the fact that it was "native copper."

What effect would it have had on the skin of the wire if the authors had turned their wire end for end during drawing? May the skin characteristics of wire be coupled with this possible alternative in drawing technique?

It is rather interesting that the authors' results indicate that single-crystal copper will not show higher electrical conductivity than multicrystal copper. If that is true, some of us are working on the wrong supposition.

C. T. EDDY.—Regarding the 102 conductivity, the wires of this conductivity were chosen only for their peculiar interest, to see whether or not they would act in the same way as the commercial wire that was used, which was furnished together with its history. These wires were cut from native mass copper which had not been melted, and it is not unusual to find wires drawn in this manner running up to 102.5 per cent. and sometimes higher in conductivity.

As for the low conductivity in copper approaching the nature of the single crystal, there is probably plenty of room for difference of opinion. However, presuming anisotropy, which is certainly possible even in an isometric material such as copper (magnetite, an isometric mineral, for instance, is anisotropic), it is possible that the orientation, which we find in the core of the hard-drawn wire, has a resistivity that corresponds to the direction of lower resistivity through the copper crystal.

R. W. DRIER.—Regarding the reversal of the drawing, we are working on that and have no results to report now.

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[5] F. W. Harris: Distribution of Tensile Strength in Hard Drawn Copper Wire. *Proc.* Inst. of Metals Div., A. I. M. E. (1928) 540.

Deoxidation of Copper with Calcium and Properties of Some Copper-calcium Alloys

By Earle E. Schumacher,* W. C. Ellis* and John F. Eckel,* New York, N. Y.

Copper-calcium alloys are of interest as materials for use in deoxidized conductors of high conductivity. That calcium is effective in deoxidizing and degasifying copper is well known. Brandenberg and Wiens[1] have described the use of calcium in the casting of sound copper and state that the deoxidation can be carried out without difficulty. The castings that they prepared were sound and sufficiently ductile to permit wire drawing. Pratt,[2] in British Patent No. 1699 (1907), has claimed the use of calcium for the deoxidation and degasification of copper. Masing[3]

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* Bell Telephone Laboratories.

[1] Editorial on method employed by Brandenberg and Wiens for deoxidation of copper with calcium. *Eng. & Min. Jnl.* (1906) **82**, 433. Full description was published in *Rev. des Produits Chimiques* (Aug. 1, 1906).

[2] A. E. Pratt: Deoxidation of Copper. British Patent No. 1699 (1907).

[3] Masing u. Haase: Herstellung von Kupferguss mit hoher Electrischer Leitfähigkeit. *Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern* (1928) **7**, 321. A partial translation of the section in regard to calcium follows:

As may be seen from Table 9, the use of calcium as a deoxidizing agent produces a cast copper of high density and high conductivity. These results of laboratory tests are not in agreement with those obtained with practical tests conducted in 1923, in which a conductivity of 50 could not be obtained by using calcium. Also, the use of calcium at that time gave rise to flaws in the surface of the castings. In consideration of these previous experiences and the result of practical tests with magnesium, we desisted from carrying out practical tests with calcium.

TABLE 9.—*Deoxidation of Copper with Calcium*

Ca, Per Cent.	Cu₂O, Per Cent.	Cu₂S, Per Cent.	Density Sand Casting	Electrical Conductivity Sand Casting	Per Cent. Conductivity* Annealed Cu Stand.
0.13	0.23		8 85	53 8	92.7
0.13		0 13	8.89	58.7	101.1
0.13	0 13	0.065	8.91	55.9	96.2

* Calculated from Masing's data using 58.0×10^4 mhos per cm. for the value of annealed copper standard at 20° C.

has described quite recently the use of calcium in producing deoxidized copper castings of high conductivity. He stated, however, that calcium was not entirely satisfactory for this purpose because the conductivity values were not consistently high, and the calcium addition gave rise to flaws in the surface of the castings.

Experiments have been conducted to determine whether the use of calcium as a deoxidizer necessarily results in serious loss of conductivity or unsatisfactory mechanical properties. A number of alloys of copper with small amounts of calcium were prepared, examined microscopically and subjected to mechanical and electrical tests. From the results obtained, which are described below, it appears that if the proper precautions are taken in melting, and if the residual calcium in the copper after deoxidation is kept below 0.1 per cent., the properties are not much changed from those of tough pitch copper.

PREPARATION OF THE ALLOYS

Alloys containing from 0.06 to 0.8 per cent. of calcium, as shown in Table 1, were prepared in an electrical resistance furnace. The calcium was added as a copper alloy containing 6.6 per cent. of calcium. The addition alloy was prepared by plunging calcium metal into molten cathode sheet copper held in an alundum-lined graphite crucible. The copper was well covered with a calcium chloride slag.

In preparing the alloys, a 3-lb. charge of cathode sheet copper was melted under charcoal in an alundum-lined graphite crucible. The addition mixture was stirred into the molten copper after the charge had been removed from the furnace. By this procedure, no appreciable amount of calcium was lost by burning at the surface. The alundum lining prevented the copper, when in the reduced condition, from dissolving impurities. Spectrographic analyses of the alloys showed but faint traces of magnesium, silicon, lead, manganese, silver and aluminum. The effect of these impurities on the conductivity is probably negligible in comparison with the effect of the larger percentage of calcium.

TABLE 1.—*Copper-calcium Alloys Prepared in the Study of the Effect of Calcium on Copper*

Melt No	Calcium Added, Per Cent.	Calcium in Alloy, by Analysis, Per Cent.	Character of Alloy
D-23	0 05	0 06	Ductile
D-25	0 10	0 10	Ductile
D-22	0.20	0.20	Ductile
D-13	0 40	0 39	Ductile
D-14	0 80		Not ductile

PROPERTIES OF ALLOYS

The alloys containing up to 0.8 per cent. of calcium were hot-rolled satisfactorily from 0.750-in. rods to 0.250-in. rods.   Those containing up to and including 0.4 per cent. of calcium were ductile and readily drawn to wire.   The ease of drawing to wire decreased with the increase in calcium content.   The alloy containing 0.8 per cent. of calcium was not sufficiently ductile for wire drawing.

Mechanical and Electrical Properties

The effect of calcium on the mechanical properties of hard-drawn copper wire is shown in Fig. 1.   The wire, 0.104 in. dia., was cold-drawn
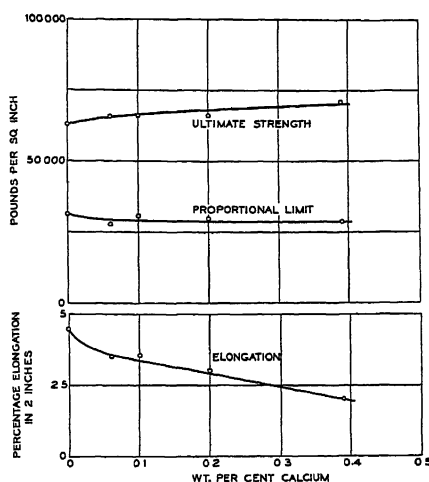
FIG. 1.—EFFECT OF CALCIUM ON MECHANICAL PROPERTIES OF HARD-DRAWN COPPER WIRE.

from 0.250-in. rod.   The ultimate strength increases slightly with calcium content, while the proportional limit remains quite constant.   The elongation in 2 in. decreases uniformly from 4.5 per cent. for tough pitch copper to 2.0 per cent. for the alloy containing 0.4 per cent. of calcium. The hardness values for these alloys increase with calcium content to some degree in both the annealed and cold-rolled condition, as is shown in Fig. 2.   Summarizing, the effect of small amounts of calcium on the mechanical properties of copper is to slightly strengthen and harden it, with a corresponding small loss in ductility.

The addition of calcium to copper is effective in producing deoxidized copper, as is shown from the results plotted in Fig. 3.   It is well known that copper containing oxygen is embrittled by annealing in hydrogen at 800° C. for 1 hr.   The alloys containing calcium were not embrittled by this treatment.   This is evident from the close agreement of the values

for ultimate strength and elongation of the corresponding alloys after air and hydrogen anneal. In Fig. 4 is shown a section of a copper-calcium wire containing 0.06 per cent. of calcium after annealing in hydrogen at
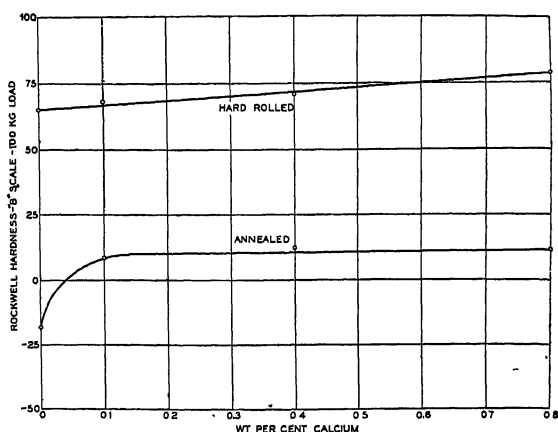
FIG. 2.—EFFECT OF CALCIUM ON HARDNESS OF HARD-ROLLED AND ANNEALED COPPER.

800° C. for 1 hr. The excess copper-calcium constituent is visible along the grain boundaries and within the crystals. The crystallite boundaries are tight, showing no evidence of embrittlement.
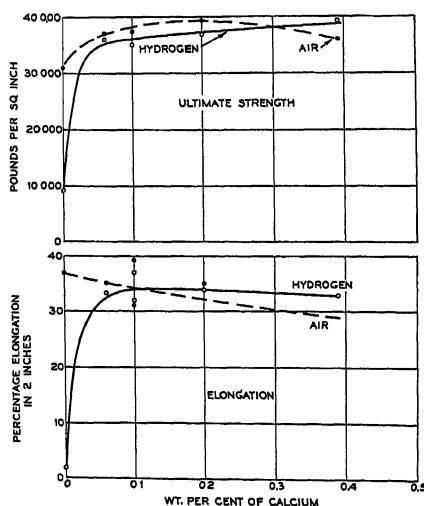
FIG. 3.—EFFECT OF ANNEALING IN HYDROGEN FOR 1 HR. AT 800° C. ON THE MECHANICAL PROPERTIES OF COPPER-CALCIUM ALLOYS.

The use of calcium for the deoxidation of copper is markedly advantageous in that the excess calcium, which alloys with the copper, has but a small effect on the conductivity. The results for annealed and

hard-drawn specimens are plotted in Fig. 5. Up to 0.2 per cent., each
0.05 per cent. of calcium remaining in the copper reduces the conductivity
approximately 1 per cent. This lowering of conductivity is decidedly less

FIG. 4.—SECTION OF COPPER-CALCIUM WIRE CONTAINING 0.06 PER CENT. CALCIUM.
ANNEALED IN HYDROGEN AT 800° C. FOR 1 HOUR. × 500.

than that encountered with most of the common elements alloyed
with copper. This is illustrated in Table 2, in which the effective
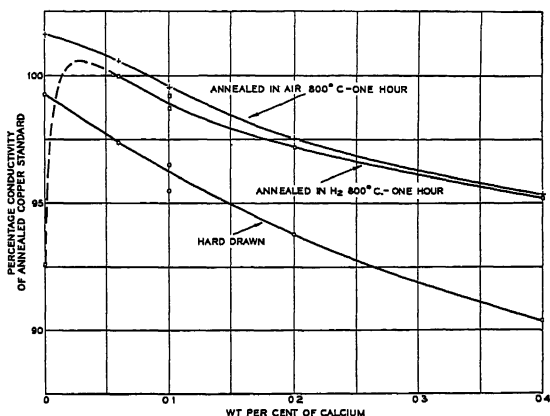
FIG. 5.—EFFECT OF CALCIUM ON CONDUCTIVITY OF COPPER.
The point on the upper curve for copper containing no calcium was obtained by
annealing at 400° C. in air.

lowering of conductivity by the addition of 1 per cent. of a number of
elements is given, together with the value for calcium extrapolated from
the data in Fig. 5.

Fig. 6.—Photomicrograph of cast copper containing approximately 0.035 per cent. oxygen. Unetched.   × 100.

Fig. 7.—Cast copper from the same melt as shown in Fig. 6 after deoxidation with calcium. No copper-copper oxide eutectic is present. The excess calcium constituent is visible. Unetched. × 100.

Fig. 8.—Same material as in Fig. 7 after being etched with NH₄OH and H₂O₂ solution. The calcium constituent is shown in its relation to the crystal grains.   × 500.
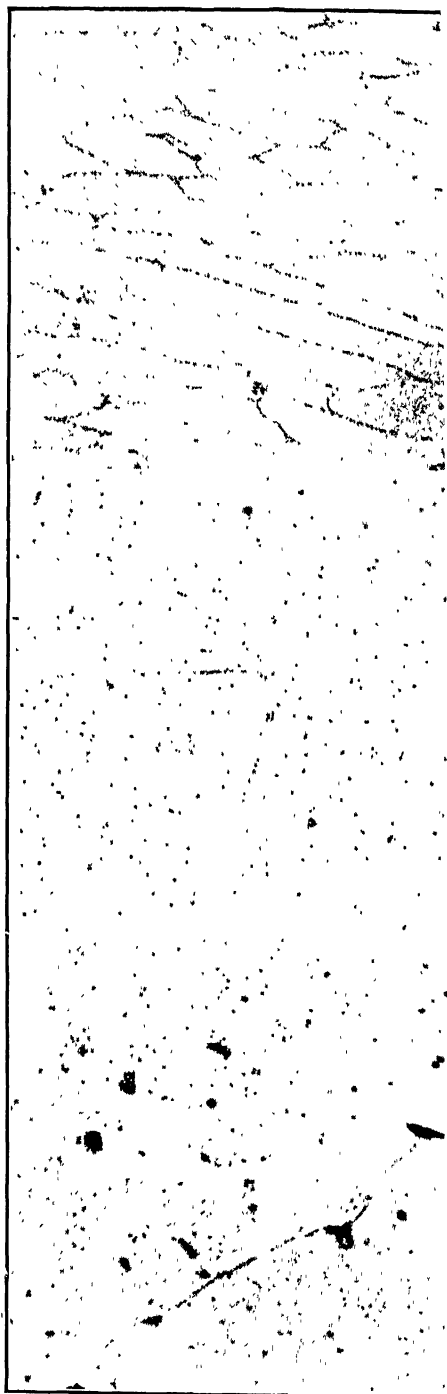
TABLE 2.—*Comparison of Effects of Certain Elements in Increasing the Resistivity of Copper*[a]

ADDED ELEMENT	INCREASE IN RESISTIVITY IN MICROHM CM. DUE TO 1 PER CENT. OF ADDED ELEMENT
Silver...............	0.10
Calcium (extrapolated)...	0.17
Zinc............	0.28
Aluminum...	1.9
Magnesium....	2.0
Silicon........	7.0
Phosphorus......	10.0

[a] W. Guertler: *Metallographie* (1924) **2**, No. 6, pt. 2, 536, Table 289.

DEOXIDATION OF COPPER CONTAINING OXYGEN BY ADDITION OF CALCIUM

To determine the commercial feasibility of deoxidizing copper by the addition of calcium, a melt was prepared of 6 lb. of cathode sheet copper to which Cu_2O was added to bring the oxygen content to approximately 0.04 per cent. One-half of the charge was poured and to the other half was added sufficient calcium to give slight excess over that thought necessary to completely deoxidize the remaining metal. This portion was then poured and the properties of the two materials were compared. Figs. 6, 7 and 8 show the microstructures of the metal from these two castings. Fig. 6 indicates the oxygen content of the first pour to be approximately 0.035 per cent. This value was obtained from a comparison with standards of known oxygen content. Figs. 7 and 8, photomicrographs of copper from the second pour to which calcium was added, reveal no evidence of oxygen. In a second experiment, a 25-lb. charge of cathode sheet copper was melted. To this was added 0.05 per cent. of calcium, a quantity indicated by previous experiments to be sufficient for deoxidation under these conditions.

The mechanical and electrical properties of the deoxidized copper from these two melts are summarized in Table 3.

TABLE 3.—*Properties of Copper Deoxidized with Calcium*
Heated 1 Hr. in H_2 at 800° C.

Description of Melt	Ultimate Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Electrical Conductivity Percentage—Annealed Copper Standard
Copper (originally containing 0.035 per cent. oxygen) deoxidized......... ...	32,000	33	100.0
Cathode sheet copper, deoxidized.......	34,300	35	100.6

The copper in each case shows a satisfactory conductivity.   The tensile strength and elongation values indicate freedom from embrittlement after annealing in reducing gases.

RELATION OF RESULTS TO STRUCTURE

The small effect of calcium in lowering the conductivity of copper indicates that the solubility in copper is slight.   This is in accordance with the equilibrium diagram of Baar[4] (Fig. 9).   This diagram shows that calcium forms a eutectic with copper.   The eutectic has a composition of 5.8 per cent. calcium and melts at 910° C.   The eutectic components are copper and $CaCu_4$.   No solubility of $CaCu_4$ in copper is indicated on the diagram.   A metallographic examination of a number of copper-rich
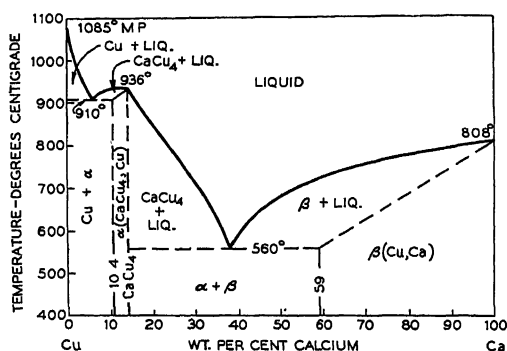
FIG. 9.—SYSTEM COPPER-CALCIUM ACCORDING TO BAAR.

copper-calcium alloys reveals the presence of the eutectic.   Fig. 10 is a section of a cast alloy containing 6.6 per cent. of calcium.   The eutectic appears as a mottled dark constituent surrounding the primary crystallites.   The eutectic is resolved at a higher magnification in Fig. 11 into characteristic lamellae.   This structure is exceedingly brittle.

In Figs. 12, 13 and 14 are shown sections of an alloy containing 0.1 per cent. of calcium in the cast, hard-drawn and annealed conditions, respectively.   In the cast structure the calcium constituent appears both within the grains and at the grain boundaries.   The section of the hard-drawn wire which was taken perpendicular to the direction of drawing is quite characteristic of this type of structure.   The photomicrograph of the annealed specimen showed recrystallization accompanied by twin formation.   The calcium constituent appears concentrated in larger dark spots than in the cast structure.

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[4] N. Baar: Über die Legierungen des Calciums mit Kupfer. *Ztsch. f. anorg. Chem.* (1911) **70**, 352.

A section of an alloy containing 0.2 per cent. of calcium is shown in Fig. 15. The calcium constituent appears as dark inclusions along the crystallite boundaries. These inclusions, at a higher magnification in Fig. 16, are resolved into a typical eutectic structure.

FIG. 10.—CAST COPPER-CALCIUM ADDITION ALLOY CONTAINING 6.6 PER CENT. CALCIUM. THE PRIMARY CRYSTALLITES ARE SURROUNDED BY A EUTECTIC STRUCTURE. ETCHED WITH NH₄OH AND H₂O₂ SOLUTION.   × 250.

FIG. 11.—SECTION OF ALLOY SHOWN IN FIG. 10 AT A HIGHER MAGNIFICATION. THE EUTECTIC IS RESOLVED INTO CHARACTERISTIC LAMELLAE. ETCHED WITH NH₄OH AND H₂O₂ SOLUTION.   × 1000.

SUMMARY OF RESULTS

1. Small additions of calcium in copper effectively deoxidize the metal without materially impairing the mechanical properties and electrical conductivity, provided the residual calcium is kept to a small percentage.

FIG. 12.—CAST COPPER-CALCIUM ALLOY CONTAINING 0.1 PER CENT CALCIUM. THE EXCESS CALCIUM CONSTITUENT IS SHOWN IN THE GRAIN BOUNDARIES AND ALSO WITHIN THE CRYSTAL GRAINS. ETCHED WITH NH_4OH AND H_2O_2. × 250.

FIG. 13.—TRANSVERSE SECTION OF HARD-DRAWN COPPER-CALCIUM ALLOY CONTAINING 0.1 PER CENT. CALCIUM. THE STRUCTURE SHOWN IS CHARACTERISTIC OF THIS TYPE OF MATERIAL. ETCHED WITH NH_4OH AND H_2O_2 SOLUTION. × 250.

FIG. 14.—TRANSVERSE SECTION OF WIRE SHOWN IN FIG. 13 AFTER ANNEALING ½ HR. AT 500° C. NUMEROUS TWINS ARE PRESENT. THE CALCIUM CONSTITUENT APPEARS AS ROUNDED PARTICLES. ETCHED WITH NH_4OH AND H_2O_2 SOLUTION. × 250.
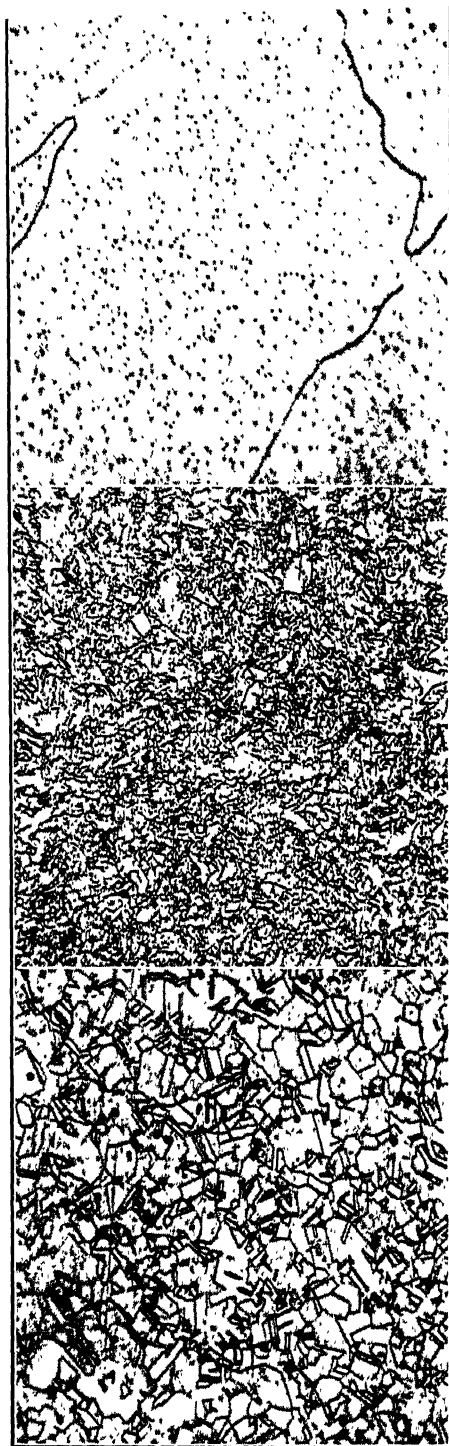
2. The deoxidation of two laboratory melts of copper with calcium resulted in material of high conductivity and good mechanical properties, which was not embrittled by annealing in reducing gases. These results
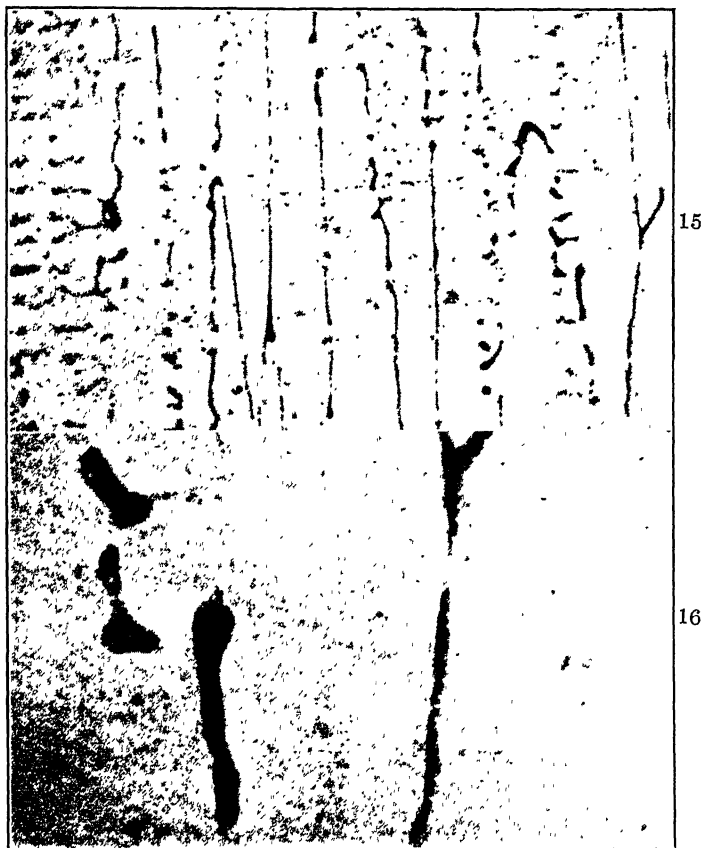
FIG. 15.—CAST COPPER-CALCIUM ALLOY CONTAINING 0.2 PER CENT. CALCIUM. THE PRIMARY COPPER CRYSTALLITES ARE SURROUNDED BY DARK INTERCRYSTALLINE MATERIAL. ETCHED WITH NH_4OH AND H_2O_2 SOLUTION. $\times$ 250.

FIG. 16.—SECTION OF FIG. 15 AT HIGHER MAGNIFICATION. THE INTERCRYSTALLINE INCLUSIONS ARE RESOLVED INTO A TYPICAL EUTECTIC STRUCTURE. ETCHED WITH NH_4OH AND H_2O_2 SOLUTION. $\times$ 1000.

indicate the possibility of producing deoxidized copper of high conductivity by this method, provided the oxygen content of the melt prior to the deoxidation is known within reasonable limits.

DISCUSSION

T. S. FULLER, Schenectady, N. Y. (written discussion).—This paper is interesting both from the standpoints of purity and of electrical conductivity. Those who have had experience with the embrittlement by hot reducing gases of copper containing

oxygen appreciate the importance of any step tending to aid the production of oxygen-free material. Fig. 5 shows graphically the effect of calcium upon the electrical conductivity of annealed and hard-drawn copper wires. Table 3 gives the electrical conductivity of two calcium-deoxidized specimens, after heating one hour in H_2 at 800° C. The information, however, does not indicate whether the conductivity measurements were made on drawn or cast material. It would be helpful to know which is the case, and if the values given are not those of the cast metal, what conductivity can reasonably be expected from castings made from copper deoxidized by the calcium process.

J. F. ECKEL.—The electrical conductivity data referred to by Mr. Fuller were determined on annealed copper wire. We have not determined the conductivity of castings made from copper deoxidized with calcium.

W. A. SCHEUCH, Chicago, Ill.—We have been doing some work along this line in conjunction with the Bell Laboratories, and if the impurities in the copper are down I see no reason why the electrical conductivity should not be up, if the copper casting has been properly heat-treated to relieve strains and permit of any physical chemical readjustment in the metal.

W. F. GRAHAM, Mansfield, Ohio.—In regard to the difference between the conductivity in the cast condition and in the wrought condition, we have found that there is an approximate difference of about 5 per cent.; that is, that the cast material of the same composition is 5 per cent. lower.

S. SKOWRONSKI, Perth Amboy, N. J.—The units of mass resistivity and volume resistivity are interrelated through the density, which is taken for copper as 8.89 grams per cubic centimeter at 20° C. Therefore, in comparing the conductivity of a casting as such as against copper wire of 8.89 density, there will be a difference in the conductivity due to the difference in density. A wire bar of 8.50 density will have a conductivity in the piece about 5 per cent. lower than a wire drawn from the same bar, since the wire will have a density of approximately 8.89.

W. A. SCHEUCH.—I think that Mr. Skowronski is right, but I see no reason for making a porous casting if the proper kind of deoxidizer can be obtained. It may be necessary to get down to the solid metal, but results should be comparable.

G. P. HALLIWELL, Pittsburgh, Pa.—Have the authors made any fatigue tests on their calcium–copper alloys and if so, how do they compare with similar tests on worked and annealed copper?

I am also interested to know whether they have used any other alkaline earth metals; barium, for instance. I have been working with this metal for some time in an attempt to make alloys of copper or nickel having a fairly high barium content. I have experienced great difficulty in obtaining sound ingots, as the barium volatilizes very rapidly during solidification, resulting in a porous nonforgeable ingot. Have the authors experienced any such difficulty with calcium? In adding the calcium to copper the authors used a calcium-rich alloy. How did they make this alloy without undue loss by oxidation?

J. F. ECKEL.—An investigation of the fatigue properties of these materials has not been made. We are conducting tests with the other alkaline earths and also with lithium, but the results are not yet complete enough to give definite conclusions. We had some trouble in dissolving the barium in the melt. In using calcium, no difficulty was encountered in the solution of the addition alloy. In preparing the copper-calcium addition alloy, copper was melted under a calcium chloride slag. The calcium was then added as metallic calcium, and some of it was lost by burning before solution was complete. The bath was stirred vigorously to insure a uniform alloy, and then poured.

S. L. Hoyt, Schenectady, N. Y.—Mr. Eckel, we had a little discussion a moment ago about the difference in conductivity between cast and drawn copper. Are there any comments you would care to interject here?

J. F. Eckel.—As stated earlier in the discussion, we have no conductivity or density data on copper castings deoxidized with calcium. It is interesting to note, though, that Masing's results (footnote 3) show an increasing conductivity with increase in density of the casting. This would indicate that density and the factors affecting density are of great importance in relation to the conductivity of castings.

S. Skowronski.—In the paper the densities of sand casting are given at 885, which would be about the gravity of the copper which had been worked. Consequently you would not expect any difference in the conductivity of the metal on account of its already high density.

E. M. Wise, Bayonne, N. J.—The effect of deoxidizers on the pouring properties is of great interest, perhaps more so in the precious-metal alloys than in copper, and while one may have a desire to use deoxidizers to accomplish certain results in the precious-metal alloys, often their use brings with it much trouble in the way of defective castings and things of that nature. The use of deoxidizers often results in retardation of grain growth, so that the annealing temperatures are raised and it, the deoxidizer, is really more trouble than it is worth. The use of calcium boride and possibly lithium would avoid some of the difficulties, which are certainly serious in cases where it is desirable to secure an absolutely sound chilled casting with a good surface.

J. F. Eckel.—We found no difficulty in pouring copper deoxidized with calcium. Analyses made on the 6-lb. melt are of interest in connection with the remarks of Mr. Skowronski. In this melt, cuprous oxide was added in sufficient quantities to bring the oxygen content to approximately 0.04 per cent. Approximately one-half of the charge was poured, 0.14 per cent. calcium was added to the other half and then that was poured. Calcium analysis of the second casting showed an excess of 0.059 per cent. calcium in the copper. Assuming that our optical analysis is correct at 0.035 per cent. oxygen, the excess calcium in the metal should be about 0.050 per cent. This figure checks with the chemical analysis. This would indicate that the calcium oxide had slagged off.

W. F. Graham.—Specimens cut from electrolytic copper ingot which meets the A. S. T. M. specification—I forget the exact number—will show about 95 per cent. conductivity, as compared with the material rolled and annealed. Is that correct?

S. Skowronski.—Yes.

W. F. Graham.—By making copper castings from that ingot under the proper conditions we have been able to attain only 95 per cent., therefore we assume that we have not added impurity or in any way changed the condition. We still have a casting of the same character in conductivity as the original chilled-cast ingot, although the casting is made in sand and not in the chilled mold. So I take that as very good evidence that the cast copper will not have more than 95 per cent. conductivity of the same composition copper in the wrought and annealed condition.

W. A. Scheuch.—Mr. Graham, what did you do to improve the quality of the second casting over the first casting? I see no reason why you should get a better casting the second time than the first time.

W. F. Graham.—I said it was the same.

W. A. Scheuch.—You should get similar results, then, as you did nothing to improve the metal.

W. F. Graham.—No, but we made a good casting from the ingot.

Alpha-phase Boundary of the Ternary System Copper-silicon-manganese

By Cyril Stanley Smith,* Waterbury, Conn.

(New York Meeting, February, 1930)

ALTHOUGH alloys of copper and silicon were examined several years ago,[1] and their excellent mechanical properties were shown, it was not until C. B. Jacobs[2] introduced manganese in small quantities to the alloys that they became of commercial importance. A few years ago The American Brass Company took over the patents and commenced to manufacture the alloy under the name "Everdur." The present study of the constitution of the ternary system was undertaken in order to reach a fuller understanding of the behavior of the alloy.

REVIEW OF PREVIOUS WORK ON THE BINARY SYSTEMS

There have been no papers published dealing with the constitution of the ternary system, although some tests of the mechanical properties have been described,[3] which indicate that there is a change in solubility with temperature.

Copper-silicon System

The copper-silicon system has been studied in detail by the author and is described in two papers published in 1928.[4] The portion of the diagram up to 8 per cent. silicon, as determined by this research, is reproduced in Fig. 1. The author's previous papers include a complete review of the work of other investigators and it is not necessary to deal further with this system here.

Copper-manganese System

The copper-manganese system has been investigated by several workers, notably Lewis,[5] Wologdine,[6] Sahmen[7] and Schemtschuschny,

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* Research Laboratory, The American Brass Co.

[1] E. S. Sperry: *Brass World* (1905) 1, 75, 413.

[2] C. B. Jacobs: U. S. Patent 1539260 (1925).

[3] Heussler: *Ztsch. f. anorg. Chem.* (1928) 171, 146.

[4] C. S. Smith: *Jnl.* Inst. Metals (1928) 40, 359.
   Trans. A. I. M. E, Inst. Met. Div. (1929) 412.

[5] Lewis: *Jnl.* Soc. Chem. Ind. (1902) 842.

[6] Wologdine: *Rev. de Mét.* (1907) 4, 25.

[7] Sahmen: *Ztsch. f. anorg. Chem.* (1908) 57, 1.

Urasow and Rykowski.[8] From the last-named research it appears that the metals form a continuous series of solid solutions, with a minimum in the liquidus at 868° C. and 30.3 per cent. manganese, as shown in Fig. 2. There is, however, much to indicate that this diagram is incorrect.

The structures of alpha and beta manganese, stable below 742° C., and between 742 and 1150° C. respectively, are very complex and it is
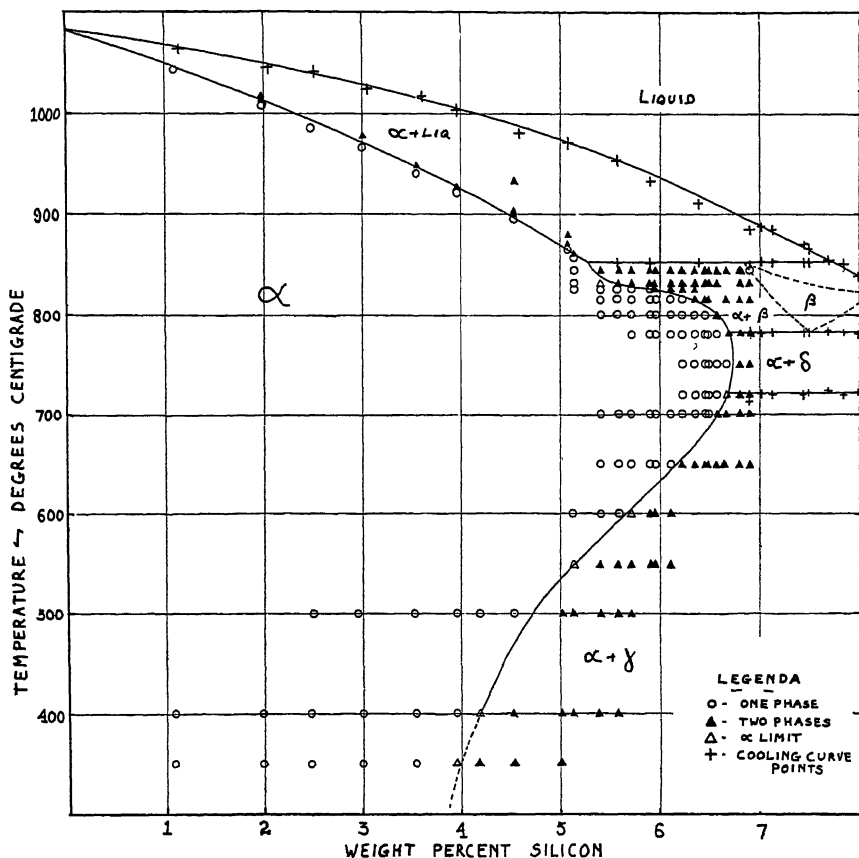
FIG. 1.—ALPHA-PHASE BOUNDARY OF THE COPPER-SILICON SYSTEM (SMITH).

quite impossible that a continuous series of solid solutions could be formed with face-centered cubic copper. Westgren and Phragmén[9] derived for alpha manganese a complicated cubic structure containing 56 atoms, and a cubic form with 20 atoms for beta manganese. Bradley and Thewlis[10] suggest a structure for alpha manganese consisting of a body-centered cube with each point represented by a tetrahedral cluster of

[8] Schemtschuschny et al.: *Ztsch. f. anorg. Chem.* (1908) **57**, 253.

[9] Westgren and Phragmen: *Ztsch. f. Phys.* (1925) **33**, 777.

[10] Bradley and Thewlis: *Proc. Roy. Soc.* (1927) **A115**, 456.

atoms. Preston[11] confirms the structure of alpha manganese determined by Bradley, and Westgren and Phragmen's structure for beta manganese.

Recently Sekito[12] has shown that the gamma form of manganese, stable above 1150° C., is face-centered tetragonal with an axial ratio of 0.940. If this is true, manganese is capable of forming a complete series of solid solutions with copper, which can be regarded as being face-centered tetragonal with an axial ratio of 1.00, but, of course, this will only apply to high temperatures, and below 1150° C. two phases must exist. X-ray work on the alloys by Bain[13] and Patterson[14] has shown
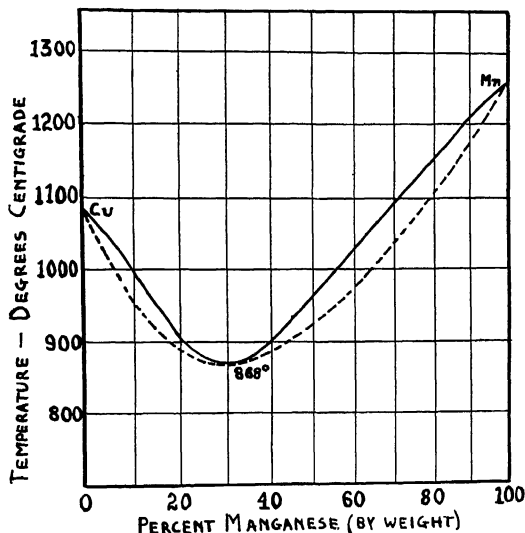
FIG. 2.—COPPER-MANGANESE EQUILIBRIUM DIAGRAM (SCHEMTSCHUSHNY).

definitely that two phases do exist, and recently the work of Gayler[15] and Corson[16] has confirmed this microscopically, although no definite attempt to fix the solubility limit has been made.[17]

To verify this point, the present author melted a number of copper-manganese alloys in alundum-lined crucibles, and cast them into rods of ½ in. dia. Sections were then cut, cold-worked by hammering, annealed for 44 hr. at 800° C. and quenched. Photomicrographs of

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[11] Preston: *Phil. Mag.* [7] (1928) **5**, 1198, 1207.

[12] Sekito: *Kinzoku no Kenkyu* [4] (1929) **6**, 200. Abst. in *Jnl.* Inst. Metals (1929) **41**, 509.

[13] Bain: *Chem. & Met. Eng.* (1923) **28**, 21; *Trans.* A. I. M. E. (1923) **68**, 625.

[14] Patterson: *Phys. Rev.* (1924) **23**, 556.

[15] Gayler: Private communication to the author, 1928.

[16] Corson: *Proc.* Inst. Met. Div., A. I. M. E. (1928) **484**.

[17] A paper by Ishiwara (World Engineering Cong., Tokyo, 1929) describing the complete system copper-manganese came to the author's attention when the present paper was being printed. Ishiwara places the solubility at 860° C. at about 32 per cent. Mn, and at 600° C. at about 22 per cent.

alloys with 67.83, 61.74, 32.59 and 11.49 per cent. copper after this treatment are shown in Figs. 3 to 6, which show clearly that the alloys are duplex in nature. The limit of solubility must be at about 30 per cent. manganese. A complete analysis of the sample containing 11.49 per cent. copper was as follows: copper, 11.49 per cent.; manganese
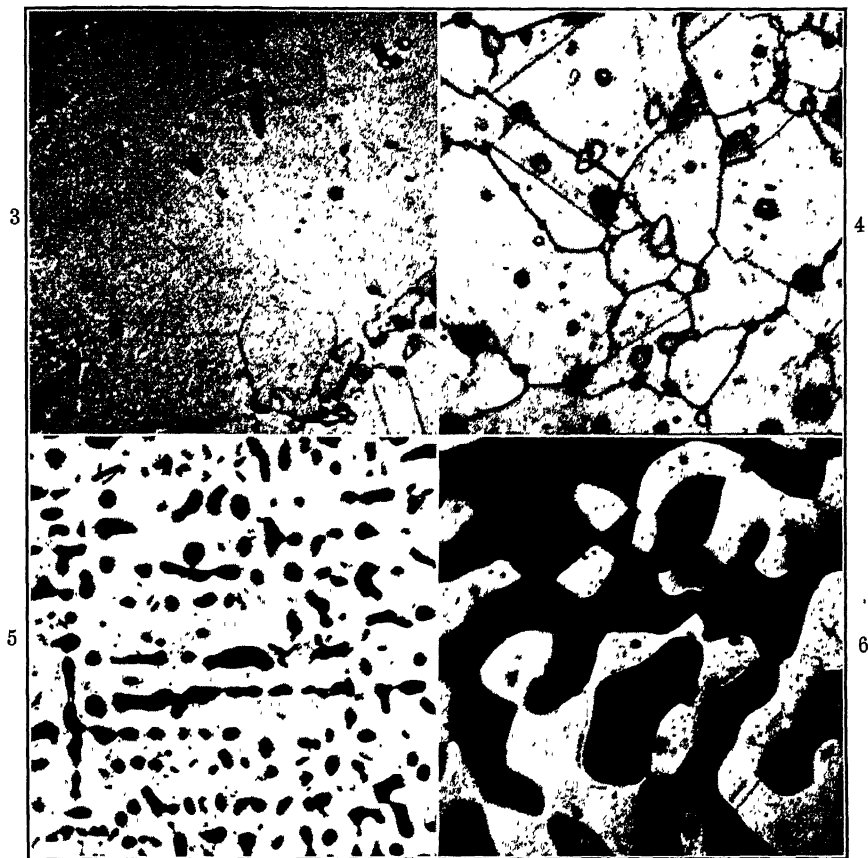
FIG. 3.—No. 226, 67.83 PER CENT. CU, 32.17 PER CENT. MN.
FIG. 4.—No. 227, 61.74 PER CENT. CU, 38.26 PER CENT. MN.
FIG. 5.—No. 230, 32.59 PER CENT. CU, 67.41 PER CENT. MN.
FIG. 6.—No. 231, 11.49 PER CENT. CU, 88.51 PER CENT. MN.
All annealed 44 hr. at 800° C. and quenched.
Etched $K_2Cr_2O_7 + H_2SO_4$. × 500.

(diff.), 87.22; iron, 1.27; carbon, 0.024. The other alloys contained iron proportionately, down to about 0.4 per cent. in the 67.8 per cent. copper alloy, but it is doubtful if this had any great affect on the structure.

It was originally intended to employ the data of Schemtschuschny and his collaborators on the liquidus and solidus in the construction of the ternary diagram, but it was found that his points did not fit in

smoothly with the liquidus surface of the ternary system as determined by the present work.   The liquidus and solidus of the binary system up to 10 per cent. manganese were therefore redetermined by a series of cooling curves and quenching experiments.   The revised diagram is shown in Fig. 7, based on data that will be found in Tables 1 and 2. The experimental methods were the same as those employed in the
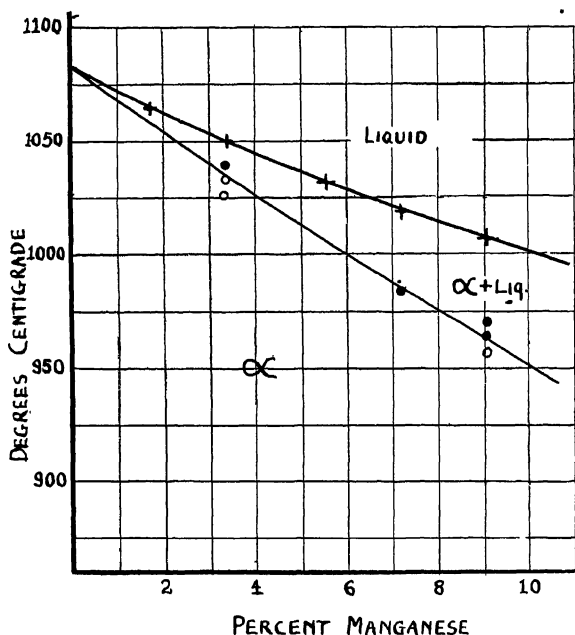
FIG. 7.—COPPER-MANGANESE EQUILIBRIUM DIAGRAM, 0 TO 10 PER CENT. MANGANESE ACCORDING TO THE PRESENT WORK.

ternary diagram and will be described later.   It will be noticed that the liquidus is concave *upwards* instead of downwards as in Schemtschu-schny's diagram, but there is not a difference of more than 20° C. between the two curves in the range studied.   The solidus line in the new diagram was determined by quenching experiments and is therefore more likely to

TABLE 1.—*Liquidus Arrests in Binary Copper-manganese Alloys*

No.	Manganese, Per Cent.	Temperature of Arrest, ° C.
185	1.72	1065
186	3.38	1050
187	5.54	1033
188	7.19	1019
189	9.01	1007
190	18.41	928
191	32.08	872

be accurate than that of Schemtschuschny, which was drawn through the very indistinct points on the cooling curves representing the completion of solidification. It should again be emphasized that the alloys in the present research contained appreciable amounts of iron.

TABLE 2.—*Microstructure of Copper-manganese Alloys Annealed at Various Temperatures in the Neighborhood of the Solidus*

No.	Manganese, Per Cent.	Microstructure	
		No Liquid, ° C.	Liquid,° C.
186	3.38	1026, 1033	1040
188	7.19		948[a]
189	9.01	957	964[a], 970

[a] Only trace of liquid present.

Manganese-silicon System

The only investigation on the manganese-silicon system is that of Doernickel[17] who gave the diagram shown in Fig. 8. This shows the existence of two compounds, Mn_2Si and $MnSi$, which form eutectics with
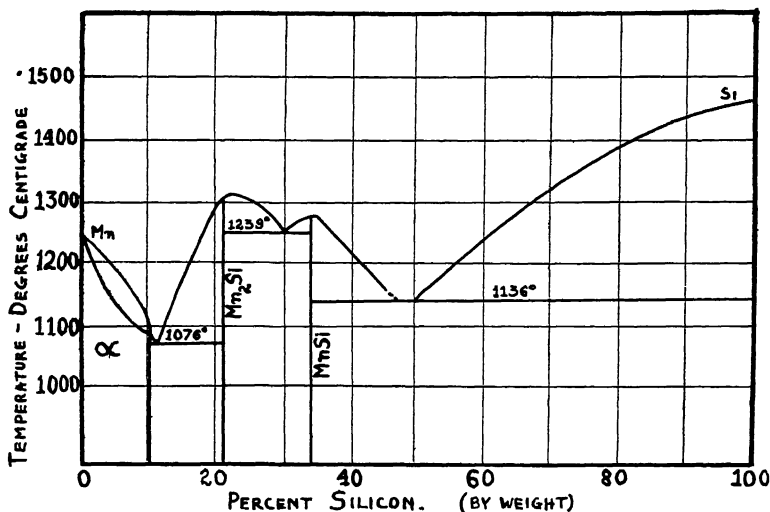
FIG. 8.—MANGANESE-SILICON EQUILIBRIUM DIAGRAM (DOERNICKEL).

each other, with a manganese-rich solid solution, and with silicon respectively.

To determine whether these two compounds did exist, alloys of manganese with 12.36, 24.23 and 35.68 per cent. silicon were melted and

[17] Doernickel: *Ztsch. f. anorg. Chem.* (1906) **50**, 117.

allowed to freeze slowly in alundum-lined crucibles. The structures agreed fairly well with Doernickel's diagram. Fig. 9 shows the alloy with 12.36 per cent. silicon to consist of manganese and eutectic, indicating a somewhat lower solubility of silicon in manganese than Doernickel's diagram indicates. The alloys corresponding approximately to Mn_2Si
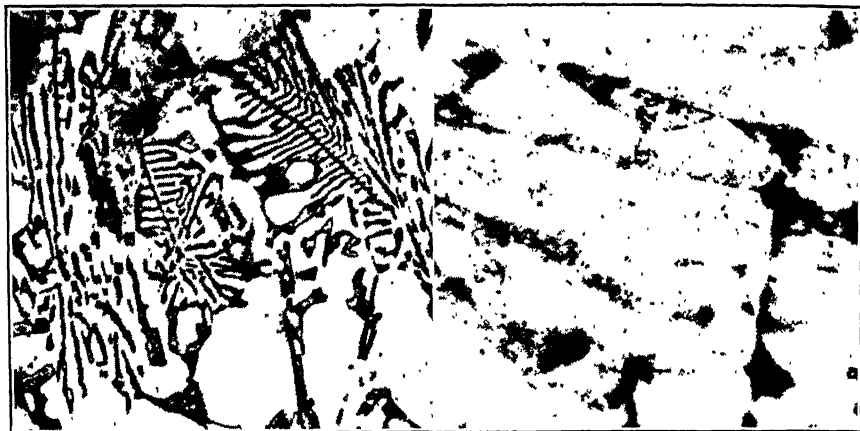
FIG. 9.—No. 201, 87.64 PER CENT. MN,   FIG. 10.—No. 202, 75.77 PER CENT. MN,
            12.36 PER CENT. SI.   24.23 PER CENT. SI.
    Slowly cooled.   Mn + Eutectic.   Slowly cooled. Mn_2Si.
            Etched HF.   × 500.   Etched HF.   × 500.

(Fig. 10) and MnSi were nearly homogeneous. X-ray diffraction patterns were taken of the alloys (Fig. 50) and these show the existence of four distinct phases as the diagram is crossed.

MATERIALS AND EXPERIMENTAL METHODS

The importance of using extremely pure materials in an investigation of this kind is well known, since it is useless to determine the position of a line with any accuracy when it is liable to be affected by the impurities present.

Electrolytic copper as commercially produced is extremely pure and was used in the present research. Commercial silicon contains between 1 and 5 per cent. of iron and other impurities, but it can readily be acid-washed by the method of Tucker[18] and obtained with a purity greater than 99.9 per cent.

The raw silicon used for the present work was of good grade, of the following analysis: silicon (balance), 99.21 per cent.; aluminum, 0.18; iron, 0.56; calcium, 0.05. This was crushed in a steel mortar to pass a 10-mesh sieve and then boiled for several hours in hydrochloric acid to

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[18] Tucker: *Jnl.* Iron and Steel Inst. (1927) **115**, 412.

which a little nitric acid had been added.   It was then filtered, washed and dried.   In Tucker's original process the silicon was next washed with hydrofluoric acid in order to remove the silica formed by the decomposition of the complex silicides.   The same result was achieved in less time by dissolving the silicon directly in molten copper, since the silica floated to the surface of the metal and was eliminated.   The proportions were such as to give directly a 12 per cent. silicon alloy, which was used in making the subsequent alloys.
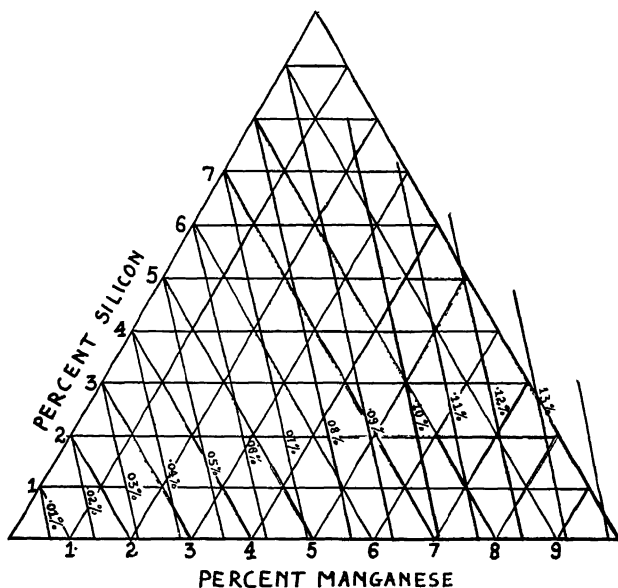
FIG. 11.—AMOUNT OF IRON IN ALLOYS USED IN PRESENT INVESTIGATION.

Manganese can be obtained in a high state of purity by the process of vacuum distillation, which was introduced by Dr. Gayler[19] of the National Physical Laboratory.   This method, although tedious, is comparatively simple to carry out, but needs a high-frequency vacuum furnace, which was not available for the present research.   The purest commercial manganese that could be obtained had to be used.   After some searching a sample was obtained containing: iron, 1.3 per cent.; carbon, 0.05; silicon, 0.60.   This was used for making the entire series of alloys.

To facilitate the introduction of exact amounts of manganese into the alloys, an intermediate alloy containing 33.3 per cent. manganese was first made up.   This alloy contained 0.47 per cent. iron.   It is realized that this is far in excess of the amount that is permissible for accurate

[19] Gayler: *Jnl.* Iron and Steel Inst. (1927) **115**, 393.

work, but it had to be tolerated; and, since the present work is only a preliminary survey, and especially because all commercial alloys must contain an even greater amount of iron, it is felt that the results are of some value in spite of this.   Fig. 11 has been prepared to show at a glance the approximate amount of iron in the alloys used in the present research.

Analytical Methods

The alloys were analyzed for copper and silicon by the same methods as those described in the author's previous papers on the copper-silicon system.   The manganese was usually taken by difference and the figure therefore bore the brunt of analytical errors and included all iron and other impurities.   The determination of silicon was slightly more inaccurate than in the binary alloys because the compound Mn_2Si is partly insoluble in the dissolving acid and was weighed as silica.   The hydrofluoric acid treatment decomposed it, and after ignition Mn_3O_4 was left with less loss in weight than if the silicon had existed as SiO_2.   This affected the results on the high-manganese alloys appreciably, but in the alloys with comparatively little manganese, on which most of the work was done, the amount of Mn_2Si was small, and there was little error in the analyses.

Thermal Analysis

The liquidus of the diagram was determined by a series of cooling curves made on alloys spaced approximately 2 per cent. apart.   Although the detail work was limited to the region with more than 90 per cent. of copper, a few alloys were made and cooling curves taken in the range with less than this amount of copper in order to make the interpretation of the results in the desired range easier.   The method of taking the cooling curves was similar to that described in the papers on the copper-silicon system, except that, owing to the affinity of manganese for carbon, the graphite crucibles were covered with a thick wash of alundum cement and the thermocouple sheaths were molded from alundum cement instead of being machined from carbon.   The charges weighed 200 g.   The copper was first melted under charcoal and to this was added the necessary amount of 12 per cent. copper-silicon alloy.   When this was melted, the charcoal was carefully skimmed from the surface and the 33 per cent. copper-manganese alloy added.   A stream of nitrogen was then led through a silica tube into the furnace to prevent undue oxidation, and the thermocouple was introduced.   The thermocouple was made of 0.040 in. chromel and alumel wires and was frequently calibrated against the following standard melting points: copper, 1083.0° C.; silver, 960.5°; silver-copper eutectic, 778.0°; aluminum, 658.9°.   The e.m.f. of the thermocouple was measured by a Leeds and Northrup type K potentiometer.

Readings were taken for plotting as inverse rate curves, a seconds clock being read every time the galvanometer reached zero after resetting the potentiometer in 0.05-mv. steps. This corresponds to a fall in temperature of about 1° C.

Annealing and Quenching Experiments

The majority of the points in the diagram were determined by a study of the microstructure of a number of alloys, which were annealed for various periods at different temperatures and quenched rapidly in water. After a preliminary survey, it was decided that by using alloys spaced 1 per cent. apart covering the entire corner of the diagram with more than 90 per cent. copper and less than 8 per cent. silicon, the important part of the alpha phase boundary would be determined. It would have been desirable to have the alloys more closely spaced, but not only would this have increased the work enormously but the added accuracy would have been largely offset by the impurities in the alloys resulting from the comparatively poor grade of manganese employed. The alloys were sometimes cast from a remelted cooling-curve ingot, but more usually were made directly from copper and the 12 per cent. copper-silicon and 33 per cent. copper-manganese alloys. They were cast in a heavy chill mold into bars ½ in. dia. and 6 in. long, and solidification was so rapid that the structure was fine enough to permit rapid homogenization on annealing. After casting, all the bars were annealed for 24 hr. at 750° C. and quenched. This removed coring and provided a suitable normal structure for subsequent heat treatment. Sections about ¼ in. long were then cut from the bars and subjected to the desired annealing treatments. If the alloys were not too brittle, they were cold-hammered to about 25 per cent. reduction in thickness in order to cause recrystallization and to enable equilibrium to be more rapidly attained on annealing. All the samples that were to be annealed at the same temperature were placed together in a heavy copper tube in an 18-in. electric tube furnace, which was specially wound and equipped with auxiliary end coils to give uniformity of temperature. A bare thermocouple rested directly against the specimens and the temperature was controlled by a Leeds and Northrup recording controller, which operated a relay controlling only a small portion of the total current necessary to heat the furnace. Very close control was possible by this method. In order to prevent excessive oxidation of the samples, the furnace was packed with charcoal and sealed with magnesia-asbestos cement. This did not entirely prevent oxidation but no trouble was caused by the thin coating of scale which was formed on the specimens. At the end of the desired time of annealing, which varied from 24 hr. at the highest temperature to a week at 450° C., the furnace was opened and the tube containing the speci-

mens was withdrawn and plunged into a bucket of water.   At least $\frac{1}{16}$ in. was filed from the surface of the specimens before polishing for examination.

The annealing for the determination of the solidus was performed in a furnace controlled by hand to within $\pm 1°$ C.   The samples had previously been homogenized by annealing and quenching, and were held at the desired temperature for 35 min.   This length of time was quite sufficient, since overheating of a solid above its melting point without fusion occurring is quite unknown.

THE DIAGRAM

The compositions of the alloys were chosen so that they could be regarded as lying on a series of sections 1 per cent. apart, parallel either to the binary copper-silicon system, the manganese increasing 1 per cent. in successive sections; or parallel to the copper-manganese side, with the
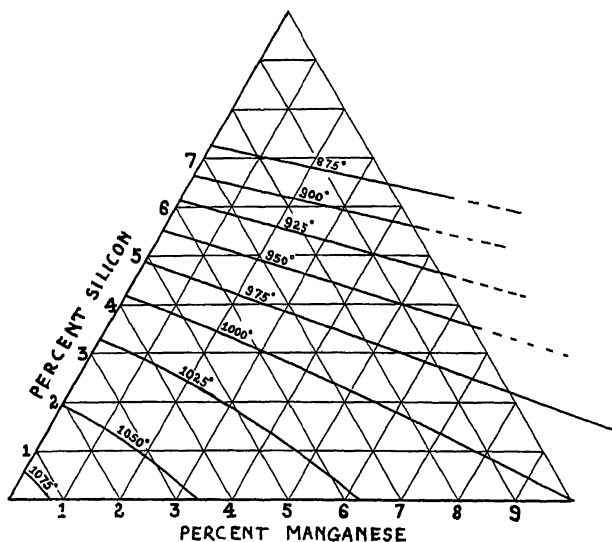
FIG. 12.—LIQUIDUS ISOTHERMS OF CU-MN-SI SYSTEM.

silicon increasing progressively.   A series of constant-temperature (isotherm) sections of the diagram were also made for every temperature of annealing used, and the three series of plots were balanced against each other until smooth curves on each set were obtained.   This gave curves which were much more likely to be accurate than those obtained by either method of plotting alone, particularly as the composition of several samples did not lie exactly in the vertical sections.

The liquidus and solidus isotherms of the system are shown in Figs. 12 and 13.   The isothermal sections are shown in Figs. 14 to 20 and the

vertical sections parallel to the copper-silicon side in Figs. 21 to 25. The copper-silicon system is the more complex and the gradual changes due
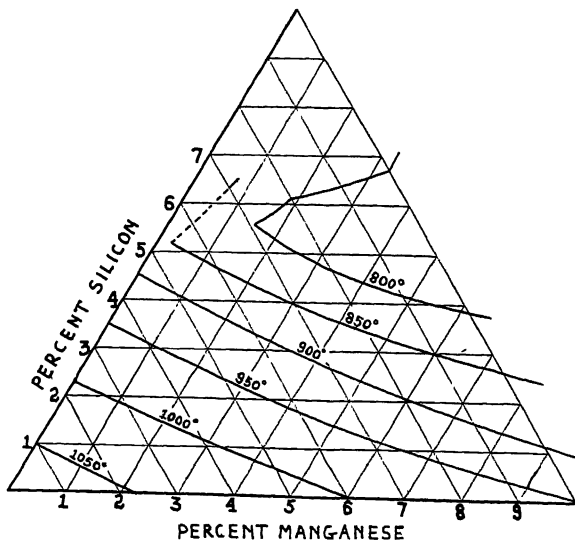
FIG. 13.—SOLIDUS ISOTHERMS OF CU-MN-SI SYSTEM.
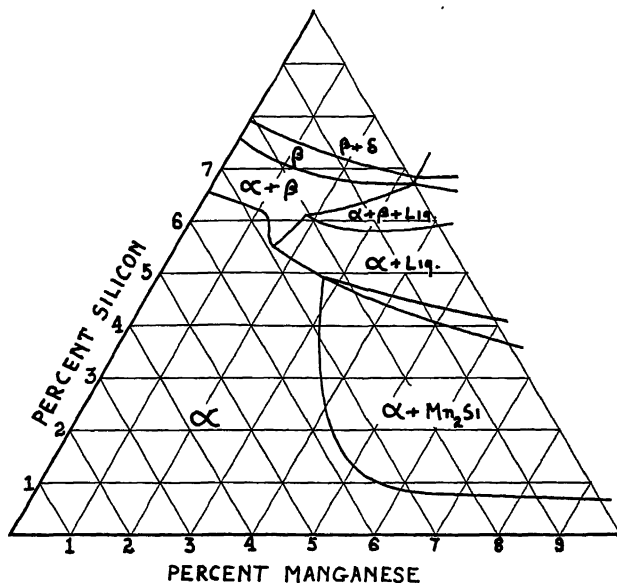
FIG. 14.—800° C. ISOTHERM OF CU-MN-SI SYSTEM.

to the addition of manganese can be more easily traced in the sections parallel to it. The sections parallel to the copper-manganese side with

progressive increase in silicon are not reproduced, since they show nothing not visible in Figs. 12 to 25.
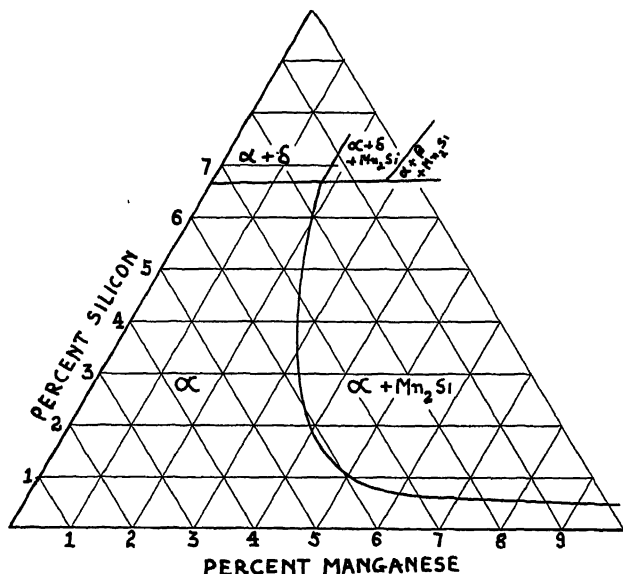
FIG. 15.—750° C. ISOTHERM OF Cu-Mn-Si SYSTEM
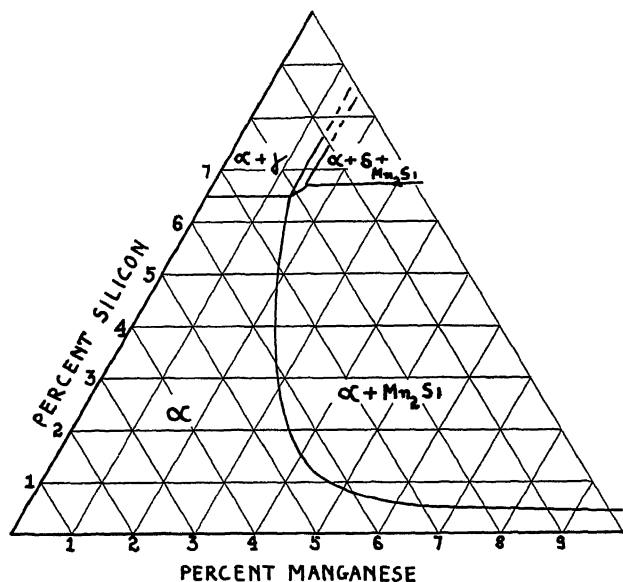
FIG. 16.—700° C. ISOTHERM OF Cu-Mn-Si SYSTEM.

To make the constitution of the system more clear, a three-dimensional model was constructed, partly of wire and partly of plaster of

Paris. Wires were used for the liquidus and solidus surfaces and for the changes in the binary copper-silicon system, but the whole space in which
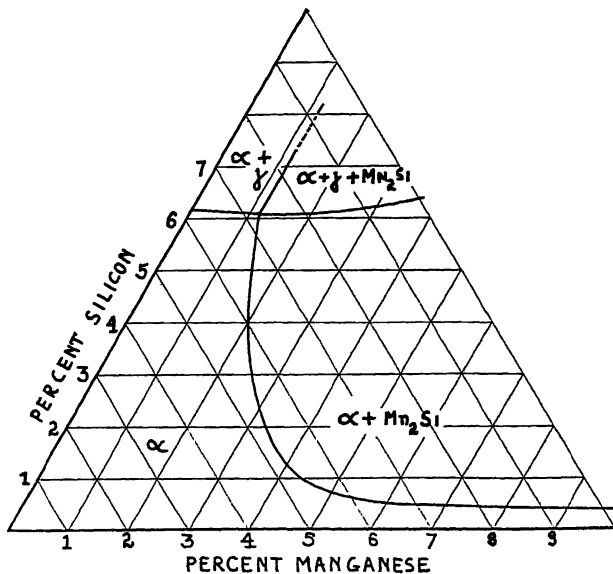
FIG. 17.—650° C. ISOTHERM OF CU-MN-SI SYSTEM.
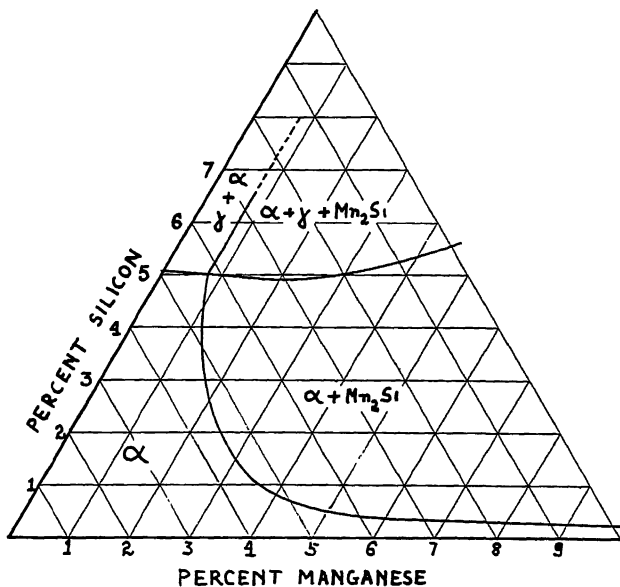
FIG. 18.—550° C. ISOTHERM OF CU-MN-SI SYSTEM.

the compound Mn_2Si existed was filled with plaster. This method of combining the two well-known methods of constructing such models is

superior to using either of them alone, for much confusion would exist if the inside field were entirely defined by wires. Photographs of this model are shown in Figs. 26 and 27.

TABLE 3.—*Summary of Cooling-curve Arrests*

Alloy No.	Silicon, Per Cent.	Manganese, Per Cent.	Temperature of Arrests			
			Primary, °C.	Secondary, °C.	Eutectic, °C.	Solid Trans., °C.
181	0.98	0.96	1062	b	b	b
182	3.00	1.01	1020	"	b	b
183	5.03	1.00	957	833	a	b
184	7.03	1.00	869	841	a	795, 693
122	1.76	2.18	1032	b	b	b
131	3.86	1.93	983	a	a	a
137	6.04	1.84	908	824, 801	a	749
141	8.74	2.39	806	a	a	698
123	1.97	3.94	1011	a	b	b
132	4.21	4.32	948	a	758	a
138	6.19	3.96	884	796	a	737
142	7.80	3.71	815	a	755	742, 668
124	2.01	5.23	995	a	a	b
133	3.75	5.85	950	773	a	a
139	5.80	5.87	865	778	758	744
134	3.75	7.85	931	782	a	a
118	7.82	7.73	785	a	762	748, 742
140	5.53	8.32	858	795	761	a
135	3.73	9.89	917	792	a	b
193	7.15	9.86	768	a	757	739, 660
127	2.03	11.27	953	a	b	b
136	3.45	11.83	901	799	a	a
128	1.92	13.08	937	801	a	a
129	2.09	15.97	909	b	b	b
130	2.11	16.69	905	809	a	a
120	4.30	19.11	837	812	b	b
192	3.83	22.77	830	814	a	a
117	2 02	26.34	863	827	a	a

[a] Arrest absent.

[b] Readings not taken at this temperature.

The temperatures of the arrests on the cooling curves are given in detail in Table 3, and the microstructures of the annealed samples in Table 4. The experimental points are. also indicated on the vertical sections of the diagram, Figs. 21 to 25.

TABLE 4.—*Microstructure of Annealed and Quenched Samples*

Temperature, °C	800	750	700	650	550	450
Time, hours....	24	24	36	48	72	168

No.	Si, Per Cent.	Mn, Per Cent.	Constituents^a					

1 PER CENT. MANGANESE SECTION

No.	Si	Mn	800	750	700	650	550	450
143	0.96	0.98	1	1	1	1	1	1
144	1.86	0 88	1	1	1	1	1	1
145	3.26	0.89	1	1	1	1	1	1 + 5^b
146	4.03	0.92	1	1	1	1	1	1 + 5
147	5 04	0.89	1	1	1	1	3 + 5^b	1 + 3 + 5
179	5.54	0.94	1	1	1	1	1 + 3 + 5	1 + 3 + 5
148	5.96	1.01	1	1	1		1 + 3 + 5	1 + 3 + 5
180	6.54	1.08	1 + 2	1	1 + 3	1 + 3	1 + 3 + 5	1 + 3 + 5
149	6 87	1.25	1 + 2	1 + 3	1 + 3	1 + 3	1 + 3 + 5	

2 PER CENT. MANGANESE SECTION

No.	Si	Mn	800	750	700	650	550	450
150	0.98	1.92	1	1	1	1	1	1
122	1.76	2.18	1	1	1	1	1	1 + 5
151	3 12	1.77	1	1	1	1	1 + 5	1 + 5
131	3.86	1.93	1	1	1	1	1 + 5	1 + 5
152	5 01	1.88	1	1	1 + 5^b	1 + 5^b	1 + 3 + 5	1 + 3 + 5
137	6 04	1.84	1 + 6	1	1 + 5	1 + 5	1 + 3 + 5	
153	6 99	1.96	2	1 + 4 + 5^b	1 + 4 + 5	1 + 3 + 5		

3 PER CENT. MANGANESE SECTION

No.	Si	Mn	800	750	700	650	550	450
154	1 17	3.12	1	1	1	1	1 + 5^b	1 + 5
155	1.98	2.93	1	1	1	1	1 + 5^b	1 + 5
156	3 08	3.12	1	1	1 + 5^b	1	1 + 5	1 + 5
157	4 07	2.99	1	1 + 5^b	1 + 5^b	1 + 5	1 + 5	1 + 5
158	5.01	3.15	1 + 6	1 + 5	1 + 5	1 + 5		1 + 3 + 5
159	5 95	3.08	1 + 2	1 + 5	1 + 5	1 + 5	1 + 3 + 5	1 + 3 + 5
160	7.13	2.81	2	1 + 2 + 5	1 + 4 + 5	1 + 3 + 5		

4 PER CENT. MANGANESE SECTION

No.	Si	Mn	800	750	700	650	550	450
161	1 01	3.82	1	1 + 5^b	1	1	1 + 5^b	1 + 5
123	1 97	3.94	1	1 + 5^b	1 + 5^b	1 + 5^b	1 + 5	1 + 5
162	3 12	3.68	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
163	4 00	4.01	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
132	4 21	4.32	1 + 6	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
164	5 02	3 92	1 + 6	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
138	6.19	3.86	1 + 6	1 + 5	1 + 5	1 + 5	1 + 3 + 5	1 + 3 + 5
165	6 77	4.34	2 + 6	1 + 2 + 5	1 + 4 + 5			

5 PER CENT. MANGANESE SECTION

Temperature, °C ...	870	800	750	700	650	550	450
Time, hours........	25	24	24	36	48	72	168

No.	Si	Mn	870	800	750	700	650	550	450
166	1 05	4.59	1	1	1 + 5^b	1 + 5^b	1 + 5^b	1 + 5	1 + 5
124	2.01	5 23	1	1 + 5^b	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
167	2 98	4 85	1 + 6^b	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
168	3 97	5 03		1 + 5	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
169	4 93	5.12		1 + 5 + 6	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5

6, 7, 8 AND 9 PER CENT. MANGANESE SECTION

Temperature,° C......	870	800	750	700	650	550
Time, hours.........	25	24	24	36	48	72

No.	Si	Mn	870	800	750	700	650	550
170	1 04	5.58	1	1 + 5^b	1 + 5	1	1 + 5	1 + 5
171	2.01	5.73	1	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
172	3 03	6.10	1 + 5 + 6	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
133	3.75	5 85		1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
173	1.05	6.65	1	1 + 5^b	1 + 5	1 + 5^b	1 + 5	1 + 5
174	1.93	6.35		1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
175	2.96	6.72	1 + 6	1 + 5	1 + 5	1 + 5	1 + 5	1 + 5
176	1.03	7.64	1 + 5^b	1 + 5	1 + 5		1 + 5	1 + 5
177	2.01	7.68	1 + 5 + 6	1 + 5	1 + 5		1 + 5	1 + 5
178	1 06	8.56	1 + 5	1 + 5	1 + 5		1 + 5	1 + 5

^a 1 = homogeneous alpha   3 = gamma   5 = Mn₂Si
  2 = beta   4 = delta   6 = liquid
^b Only a trace of this constituent present.

The addition of manganese to the copper-silicon system results in a gradual depression of the liquidus and a more marked depression of the solidus. The peritectic reaction $\alpha + \text{Liq.} \rightleftarrows \beta$ at 5.25 per cent. silicon and 852° C. in the binary system forms a trough in the ternary system, and the temperature falls rapidly to 760° C. at 2.5 per cent. manganese and 5.8 per cent. silicon where the binary valley meets the plane of the ternary eutectic or peritectic that is formed, probably between alpha, beta, and Mn$_2$Si. The exact nature and composition of the quaternary point is not known, but from the relative slope of the solidus and liquidus
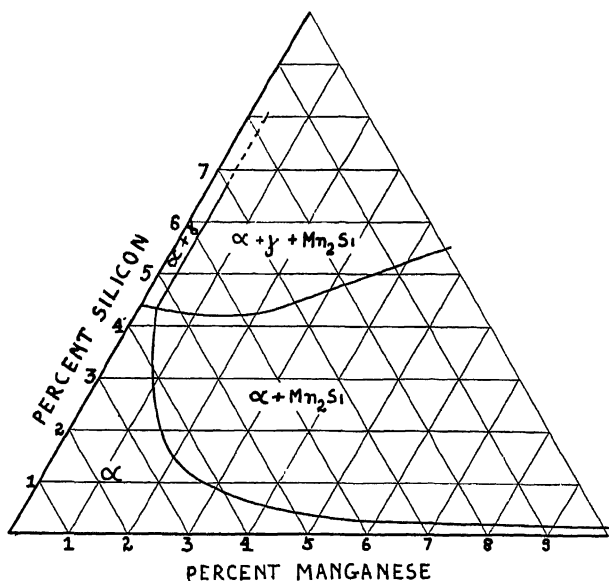
FIG. 19.—450° C. ISOTHERM OF CU-MN-SI SYSTEM.

surfaces, it is probably in the neighborhood of 7.5 per cent. silicon and 9 per cent. manganese, at a temperature of 760° ± 5° C. A single alloy was made up containing 7.15 per cent. silicon and 9.86 per cent. manganese, and its cooling curve (Fig. 28C) showed primary solidification at 768° C., with a constant temperature arrest at 757° C. The microscope showed a few needles of primary Mn$_2$Si, indicating that the eutectic composition had been slightly exceeded. Fig. 29 is of an alloy containing slightly more manganese (6.69 per cent. silicon, 10.07 per cent. manganese) and has proportionately more Mn$_2$Si.

If beta is one of the phases reacting at the quaternary point, there must also exist a binary eutectic or peritectic reaction between both Mn$_2$Si and alpha, and Mn$_2$Si and beta. No information whatever was obtained regarding the latter, but an arrest presumably due to the Mn$_2$Si-alpha binary eutectic was present in the cooling curves of all

alloys in the area between the lines joining copper with the quaternary point and Mn_2Si, respectively, a typical example being shown in Fig. 28B. An alloy with 23 per cent. manganese and 3.8 per cent. silicon (Fig. 30) was evidently a little beyond the binary eutectic, for it contained large needles of primary Mn_2Si.
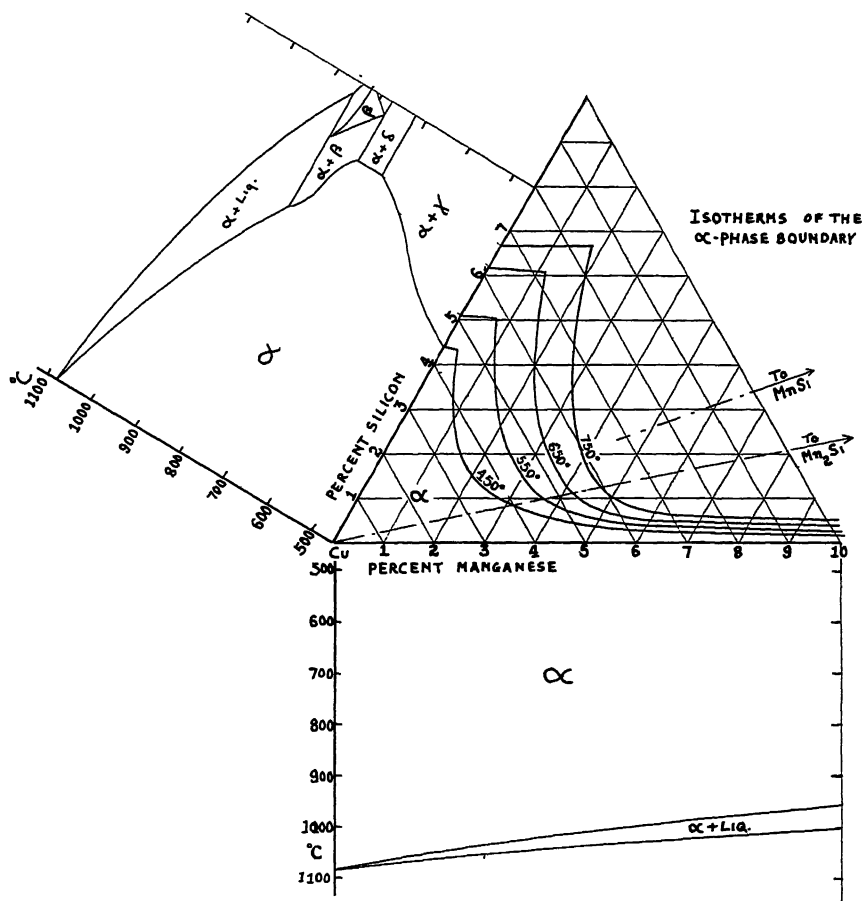
FIG. 20.—ISOTHERMS OF ALPHA-PHASE BOUNDARY AND THE BINARY SYSTEMS.

The field alpha + Mn_2Si + liquid in the diagram has been drawn in largely because it is theoretically necessary. The microstructure of the alloys in this range is rendered very indistinct by the fact that the small particles of Mn_2Si act as nuclei for the formation of drops of liquid, and it is difficult to decide whether any Mn_2Si existed at the moment of quenching or not. In the case of the alpha + beta + liquid field, the relative proportions were much larger and the constituents more distinct.
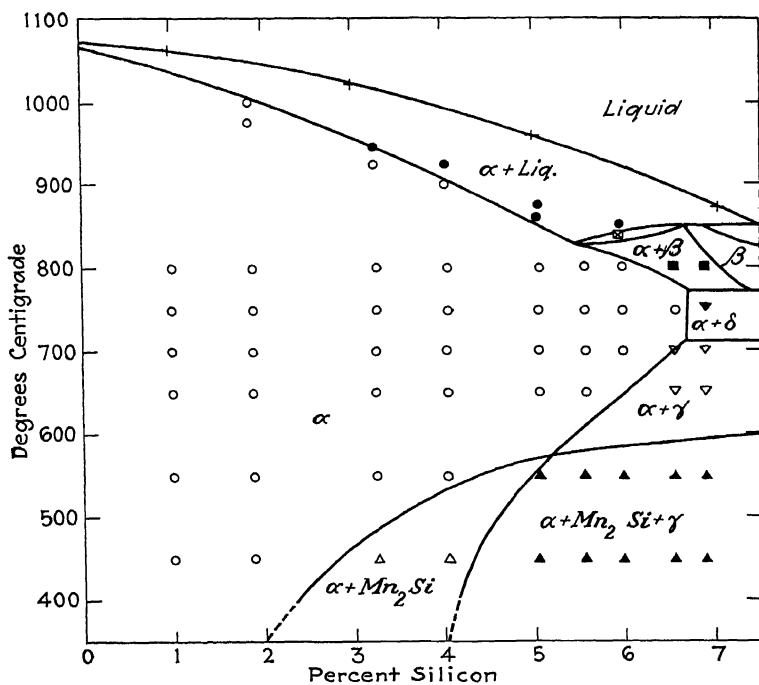
FIG 21.—SECTION OF TERNARY CU-MN-SI DIAGRAM AT 1 PER CENT. MANGANESE.
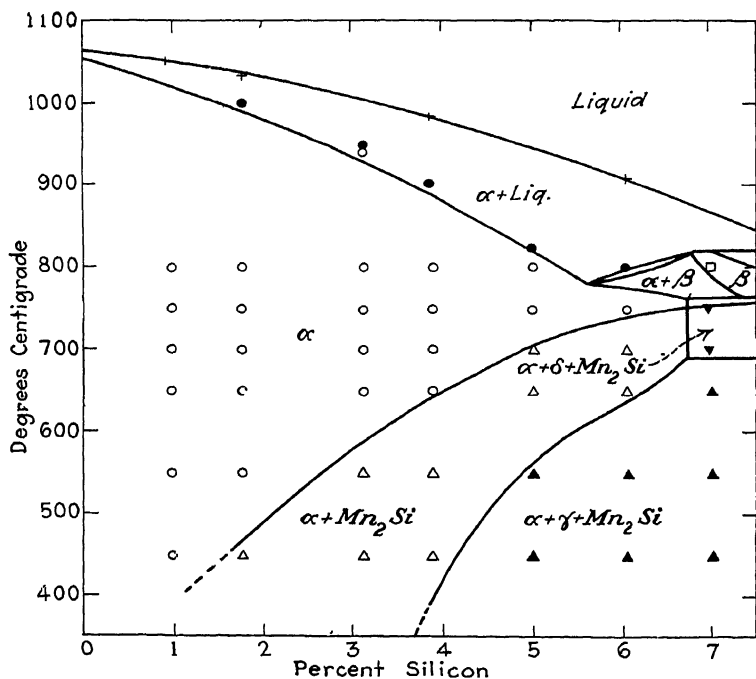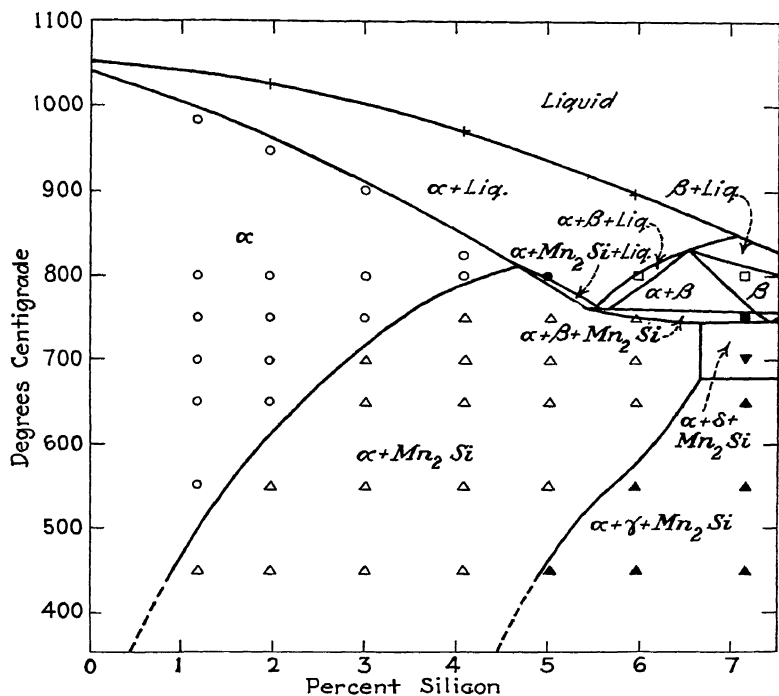
FIG. 23.—SECTION OF TERNARY DIAGRAM AT 3 PER CENT. MANGANESE.
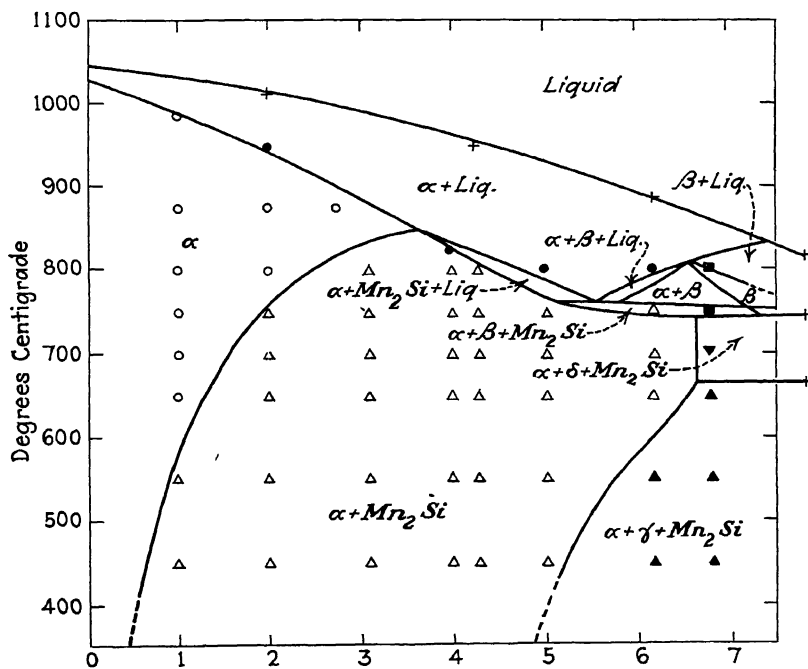
The field alpha + beta + Mn₂Si has been shown in the diagram as extending completely under the plane of the ternary eutectic, although the quenched samples had this structure only on the high-silicon side, beta being absent directly under the horizontal plane. The phase rule requires a three-phase field in this part, and it has accordingly been drawn in. The whole of this part of the diagram is tentative, however.

The temperature of the $\beta \rightleftarrows \alpha + \delta$ eutectoid change in the binary copper-silicon system is depressed by the addition of manganese, as also is the $\alpha + \delta \rightleftarrows \gamma$ peritectoid. Normally occurring at 782° and 726° C.,
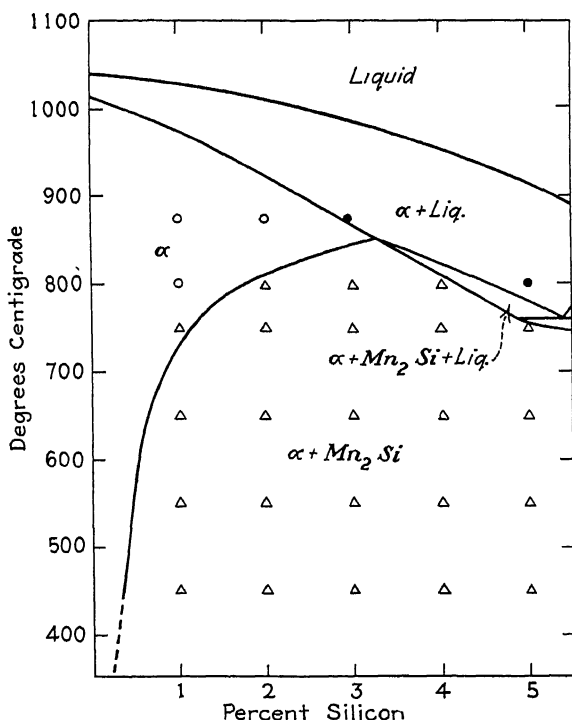
FIG. 25.—SECTION OF TERNARY DIAGRAM AT 5 PER CENT. MANGANESE.

in alloy 142, containing 7.80 per cent. silicon and 3.71 per cent. manganese, these two changes were observed at 742° and 668° C. respectively Except for this lowering of temperature and the appearance of Mn₂S beyond a certain point, the phases of the copper-silicon system exist more or less unchanged by the addition of manganese. Thus, Figs. 31, 32 and 33 show the existence of alpha, beta and gamma in an alloy containing 6.54 per cent. silicon and 1.08 per cent. manganese, in exactly the same form as they exist in a similar alloy without manganese. At low temperatures, however, Mn₂Si makes its appearance as very small
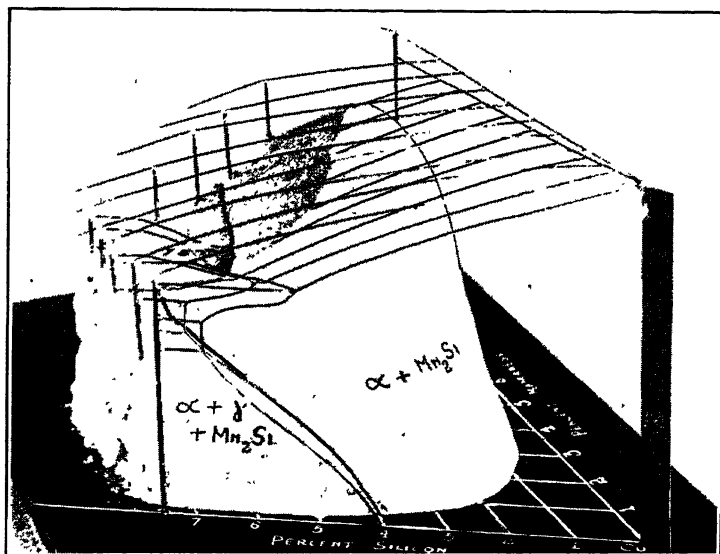
FIG. 26.—SOLID MODEL OF TERNARY EQUILIBRIUM DIAGRAM.
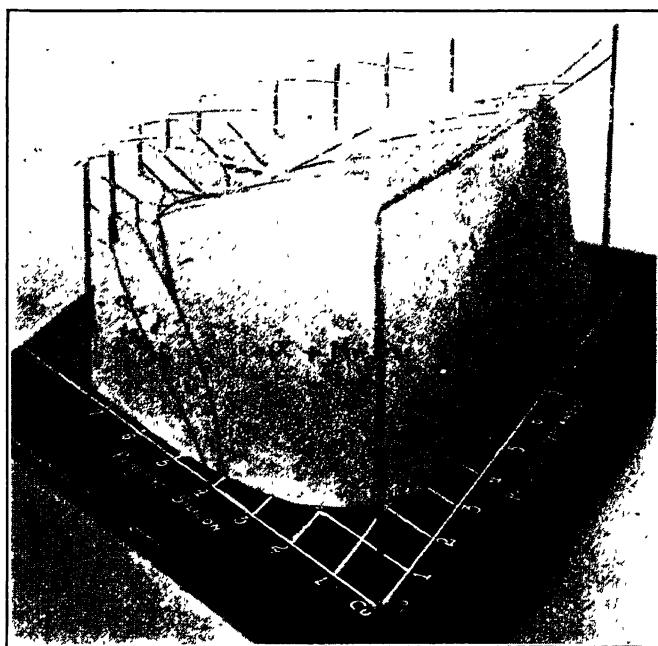
FIG. 27.—SOLID MODEL OF TERNARY DIAGRAM.
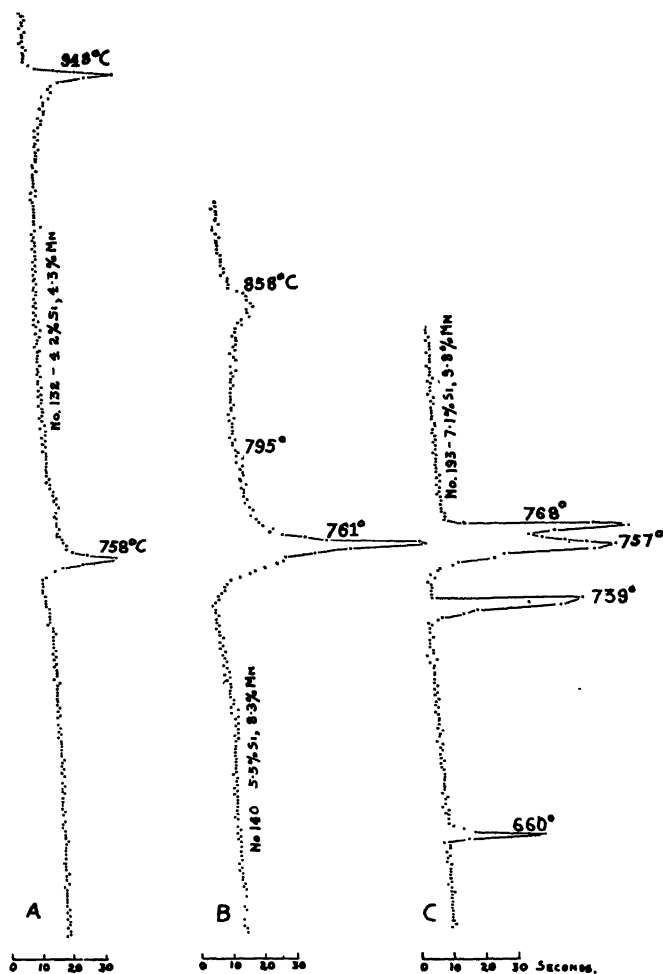
FIG. 28.—TYPICAL COOLING CURVES OE COPPER-MANGANESE-SILICON ALLOYS.

FIG. 29.—No. 194, 6.69 PER CENT. SI, 10.07 PER CENT. MN.   CAST.   MN₂SI +
EUTECTIC.   × 1000.

FIG. 30.—No. 192, 3.83 PER CENT. SI, 22.77 PER CENT. MN.   COOLING CURVE
INGOT.   × 1000.

FIG. 31.—No. 180, 6.54 PER CENT. SI, 1.08 PER CENT. MN.   QUENCHED 800° C.
α + DECOMPOSED β.   × 500.

FIG. 32.—No. 180, 6.54 PER CENT. SI, 1.08 PER CENT. MN.   QUENCHED 750° C.
HOMOGENEOUS α.   × 500.

FIG. 33.—No. 180, 6.54 PER CENT. SI, 1.08 PER CENT. MN.   QUENCHED 650° C.
α + γ.   × 100.

FIG. 34.—No. 180, 6.54 PER CENT. SI, 1.08 PER CENT. MN.   QUENCHED 550° C.
α + γ + MN₂SI.   × 500.

All samples etched with K₂Cr₂O₂ and H₂SO₂

particles scattered at random over the entire structure (Fig. 34). Figs. 35 to 38 are of an alloy containing 7.13 per cent. silicon and 2.81 per cent. manganese, which is pure beta at high temperatures, but at lower temperatures contains Mn_2Si, first with alpha and beta (Fig. 36), then with alpha and delta (Fig. 37), and lastly with alpha and gamma (Fig. 38). Fig. 39 shows another alloy, 6.99 per cent. silicon, 1.96 per cent. manganese quenched from 700° C. The structure consists of a few crystals of Mn_2Si with partly decomposed delta in a groundmass of alpha.

The presence of liquid in the samples at the moment of quenching was always unmistakable. It first appeared around the grain boundaries and later as small spots throughout the grains. Figs. 40 and 41 show this well, while Fig. 42 shows at higher magnification the structure of the quenched liquid areas.

It should be mentioned that on account of the pale blue color of most of the constituents even after etching, it was necessary to photograph the specimens with red light (Wratten "F" filter) and a panchromatic plate. This makes the alpha white in the prints, and delta, gamma and Mn_2Si somewhat darker. Beta always decomposes on quenching, resulting in a coarse structure, while delta shows a partial fine decomposition and gamma is quite structureless. Mn_2Si is bluish gray, much darker than delta or gamma, and in the cast state exists as coffin-shaped needles or hexagons, often in skeleton form, with a hole in the center (Figs. 29 and 30). In the annealed alloys the particles become more or less rounded, as shown in Figs. 43 and 44; while if it is precipitated from alpha by annealing at a low temperature the constituent forms strings of extremely fine particles along definite crystallographic planes, or slip bands if the alloy has been cold-worked. Figs. 45 to 48 show the appearance of the precipitate under various condition, while Fig. 49 shows precipitation of Mn_2Si with a small amount of gamma. With a much larger amount of gamma, the structure has already been seen in Figs. 34 and 38.

Fig. 35.—No. 160, 7.13 per cent. Si, 2.81 per cent. Mn. Quenched 800° C. Decomposed β. × 100.

Fig. 36.—No. 160, 7.13 per cent. Si, 2.81 per cent. Mn. Quenched 750° C. $\alpha + \beta + Mn_2Si$. × 500.

Fig. 37.—No. 160, 7.13 per cent. Si, 2.81 per cent. Mn. Quenched 700° C. $\alpha + \delta + Mn_2Si$. × 500.

Fig. 38.—No. 160, 7.13 per cent. Si, 2.81 per cent. Mn. Quenched 650° C. $\alpha + \gamma + Mn_2Si$. × 500.

Fig. 39.—No. 153, 6.99 per cent. Si, 1.96 per cent. Mn. Quenched 700° C. $\alpha + \delta + Mn_2Si$. × 500.

Fig. 40.—No. 158, 5.01 per cent. Si, 3.15 per cent. Mn. Quenched 800° C. $\alpha + $ liquid. × 100.

All samples etched with $K_2Cr_2O_7$ and H_2SO_4.

FIGS. 35 to 40.
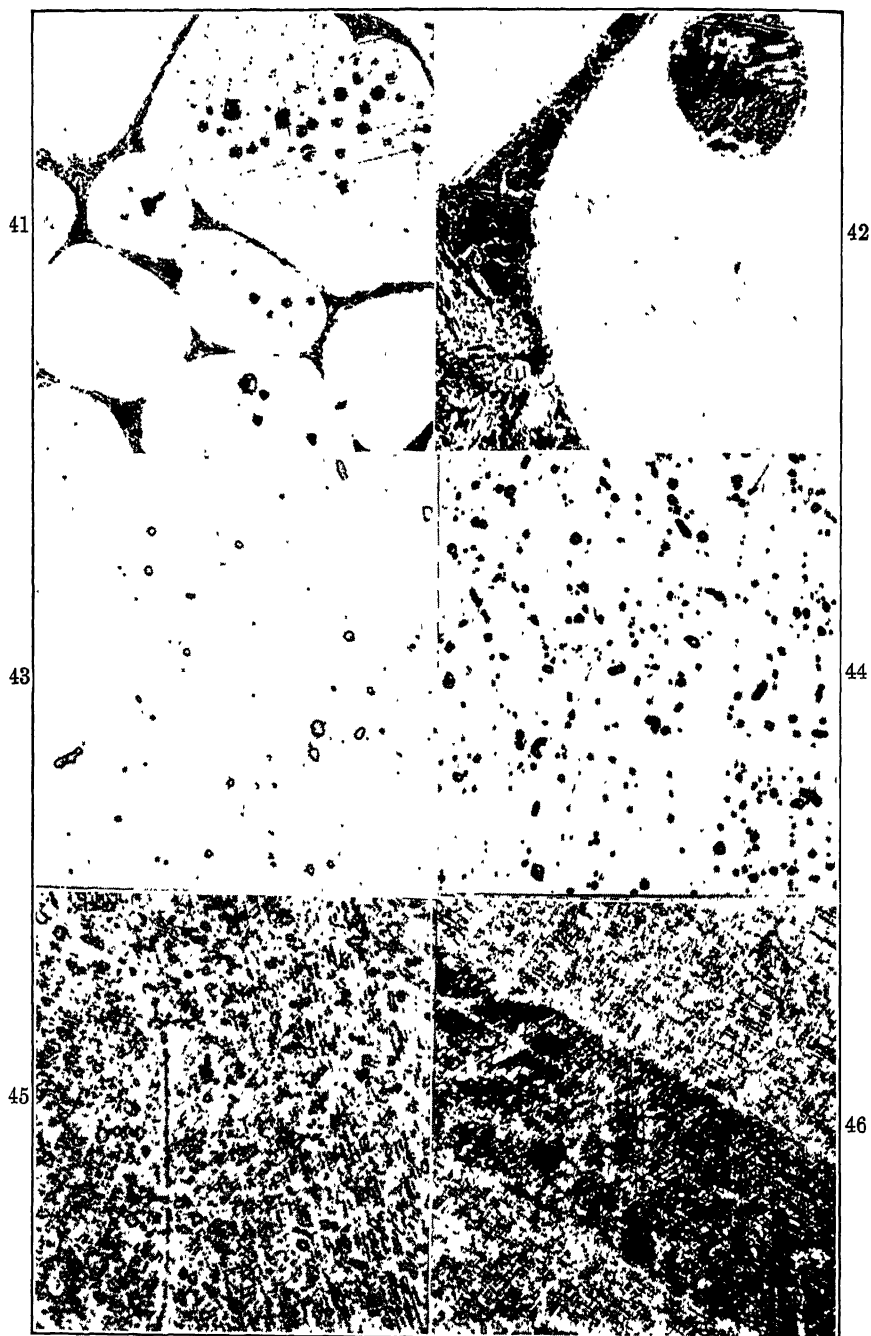
FIGS. 41 to 46.

FIG. 41.—No. 164, 5.02 PER CENT. SI, 3.92 PER CENT. MN. QUENCHED 800° C. α + LIQUID. × 100.

FIG. 42.—No. 169, 4.93 PER CENT. SI, 5.12 PER CENT. MN. QUENCHED 800° C. α + LIQUID. × 500.

FIG. 43.—No. 133, 3.75 PER CENT. SI, 5.85 PER CENT. MN. QUENCHED 800° C. α + Mn_2Si. × 500.

FIG. 44.—No. 138, 6.19 PER CENT. SI, 3.86 PER CENT. MN. QUENCHED 700° C. α + Mn_2Si. × 500.

FIG. 45.—No. 169, 4.93 PER CENT. SI, 5.12 PER CENT. MN. QUENCHED 550° C. α + Mn_2Si. × 500.

FIG. 46.—No. 169, 4.93 PER CENT. SI, 5.12 PER CENT. MN. QUENCHED 450° C. α + Mn_2Si. × 500.

FIG. 47.—No. 178, 1.06 PER CENT. SI, 8.56 PER CENT. MN. QUENCHED 450° C. α + Mn_2Si. × 500.

FIG. 48.—No. 156, 3.08 PER CENT. SI, 3.12 PER CENT. MN. QUENCHED 450° C. α + Mn_2Si. × 500.

FIG. 49.—No. 152, 5.01 PER CENT. SI, 1.88 PER CENT. MN. QUENCHED 450° C. α + γ + Mn_2Si. × 500.

Identification of Mn₂Si

It seemed probable from a study of the manganese-silicon diagram that the blue constituent that appears in the alloys when enough manganese is added is Mn_2Si rather than any of the other constituents in the binary series. To establish this point definitely, some of the blue constituent was separated and its X-ray diffraction pattern obtained and compared with a sample of a pure fused manganese-silicon alloy corresponding approximately to Mn_2Si.

The constituent was found to be practically insoluble in a mixture of nitric and sulfuric acids, which dissolved the remainder of the alloy and left a residue consisting of gelatinous silica and the blue constituent. The silica had no affect on the diffraction pattern. Alloys were treated containing 7.15 per cent. silicon and 9.8 per cent. manganese; and 3.75 per cent. silicon and 5.85 per cent. manganese. The former was in the cast state and contained a small quantity of the constituent in the primary form, while the latter had been annealed for 1 week at 450° C. to produce maximum precipitation. The residues from each were washed and dried, and their diffraction patterns were obtained, using the standard General Electric Co. apparatus with molybdenum $K\alpha$ radiation. At the same time patterns were obtained of pure manganese-silicon alloys containing 12.36, 24.23 and 35.65 per cent. silicon, melted and allowed to cool slowly. The diffraction patterns of both insoluble residues were identical with the 24.23 per cent. silicon alloy, as regards both the intensity and position of the lines. This alloy corresponds closely to Mn_2Si (20.19 per cent. silicon) and the identification is quite positive. The other two alloys, which correspond roughly to manganese saturated with silicon and the compound MnSi respect'vely, had totally different patterns. Prints from the films obtained are shown in Fig. 50, mounted together for direct comparison.

SUMMARY

By means of a series of cooling curves and the microscopic examination of a large number of annealed and quenched samples, the equilibrium relations of the ternary alloys containing more than 90 per cent. copper have been determined. The addition of manganese causes a depression of the temperatures of the reactions in the binary copper-silicon system, until at 2.5 per cent. manganese the beta peritectic reaction has fallen to 760° C., at which temperature there is a quaternary reaction with MN_2Si. The solubility of Mn_2Si decreases rapidly as the temperature falls, until at 450° C. it is less than 0.5 per cent. with 4 per cent. or more of either manganese or silicon.
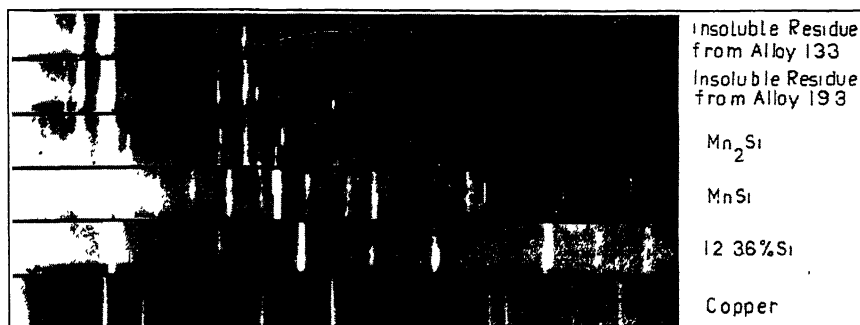
FIG. 50.—X-RAY DIFFRACTION PATTERNS OF MN-SI ALLOYS, COMPARED WITH MN₂SI OBTAINED FROM COPPER-RICH ALLOYS.

DISCUSSION

O. W. ELLIS, Toronto, Ont.—I wonder if Dr. Smith could give us any information as to the results of quenching and aging on the hardness and mechanical properties of some of these very interesting copper-silicon-manganese alloys.

C. S. SMITH.—Corson[20] and Gregg[21] have mentioned the possibility of hardening these alloys, while Heusler[22] has a patent covering a certain range of the ternary alloys. I have myself done a small amount of work with a single alloy containing 4 per cent. silicon and 2.5 per cent. manganese. The hardness of this alloy increases considerably on annealing at 450° C. following a quench from 800° C., but the tensile strength increases only a small amount and the elongation decreases considerably. I have not investigated the complete series, but I am not of the opinion that useful age-hardenable alloys will be found near the copper end of the series.

[20] Proc. Inst. of Metals Div., A. I. M. E. (1928) 483.
[21] Trans. A. I. M. E., Inst of Metals Div. (1929) 409.
[22] U. S. Patent No. 1692936 (1928).

The Alpha-beta Transformation in Brass

By Albert J. Phillips,* Waterbury, Conn.

When brasses containing from 61 to 62.5 per cent. copper are very rapidly cooled from temperatures near their melting point to below 0° C., unusual results are obtained. These results are quite unexplainable from a consideration of the old copper-zinc constitutional diagram but they can be satisfactorily explained by means of the diagram revised by Genders and Bailey[1] (Fig. 1).

Experiments on a 60/40 Brass

If an alloy containing 60 per cent. copper is heated to any temperature between approximately 760° C. and its melting point, it will consist entirely of beta. Upon slowly cooling, alpha will start to separate just below 760° C. Since this alpha will contain nearly 65 per cent. copper, the beta will be impoverished by its separation. As the temperature decreases the composition of the separating alpha will approach approximately 61 per cent. and the beta in contact with the alpha will maintain an equilibrium composition approaching 54.5 per cent. copper. If the rate of cooling is extremely slow, especially at the lower temperatures, stable equilibrium will be established by diffusion through the alpha and beta so that eventually 85 per cent. of the alloy will consist of alpha containing 61 per cent. copper, while 15 per cent. will be beta containing 54.5 per cent. copper. With a faster cooling rate diffusion cannot keep apace and the constituents will be cored, the alpha varying from 65 to 61 per cent. copper and the beta from 60 to 54.5 copper. In this case the amount of alpha will be less than 85 per cent. and the beta will be increased correspondingly. The general structure thus obtained is illustrated in Fig. 2.

When a more rapid rate of cooling is effected by quenching in water, the alloy is retained largely in the beta form. However, the crystals of beta are usually outlined with dark fringes which at high magnifications are found to be very fine alpha-beta structures almost martensitic in appearance. The separation of this fringe can be greatly suppressed

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* Metallurgist, Scovill Manufacturing Co.
[1] R. Genders and G. L. Bailey: The Alpha-phase Boundary of the Copper-zinc System. *Jnl.* Inst. Metals (1925) **33,** 213.

if the quenching medium is a brine solution maintained at −5 to −10° C. A structure thus obtained is illustrated in Fig. 3.

EXPERIMENTS ON A 62/38 BRASS

An alloy containing 62 per cent. copper can be made all beta by heating to about 850° C. Upon slowly cooling from this temperature
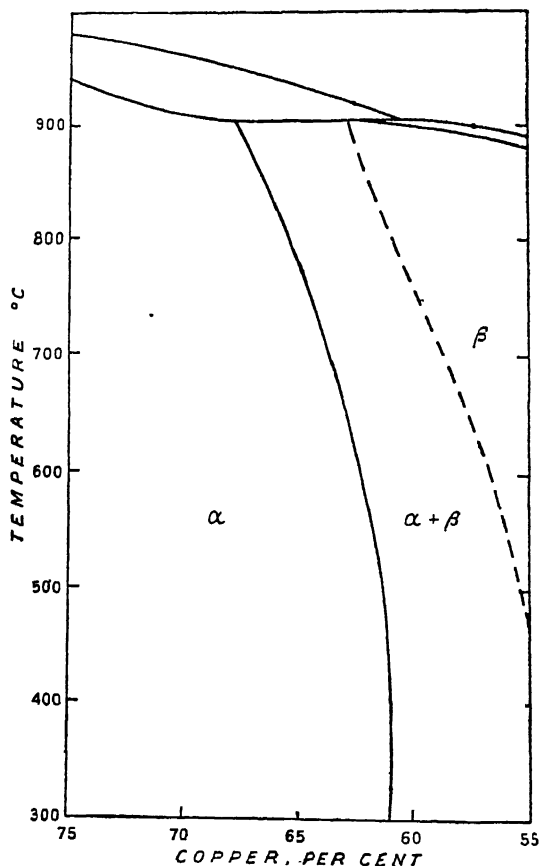
FIG. 1.—SECTION OF THE COPPER-ZINC EQUILIBRIUM DIAGRAM AS REVISED BY GENDERS AND BAILEY.

alpha having an initial composition of above 66.5 per cent. copper will immediately start to separate. If the cooling rate is slow enough for perfect diffusion, the beta, which will progressively decrease in copper to as low as 56 per cent., will finally be entirely absorbed by the alpha. Thus, by changing the temperature this alloy will have been converted from stable beta to equally stable alpha. A cooling rate of more than a degree or two an hour will prevent this conversion, for without time for

complete diffusion the precipitated alpha will have a cored structure, the outer rim of which will finally be in equilibrium with beta of 54.5 per cent. copper. The structure thus obtained will resemble that
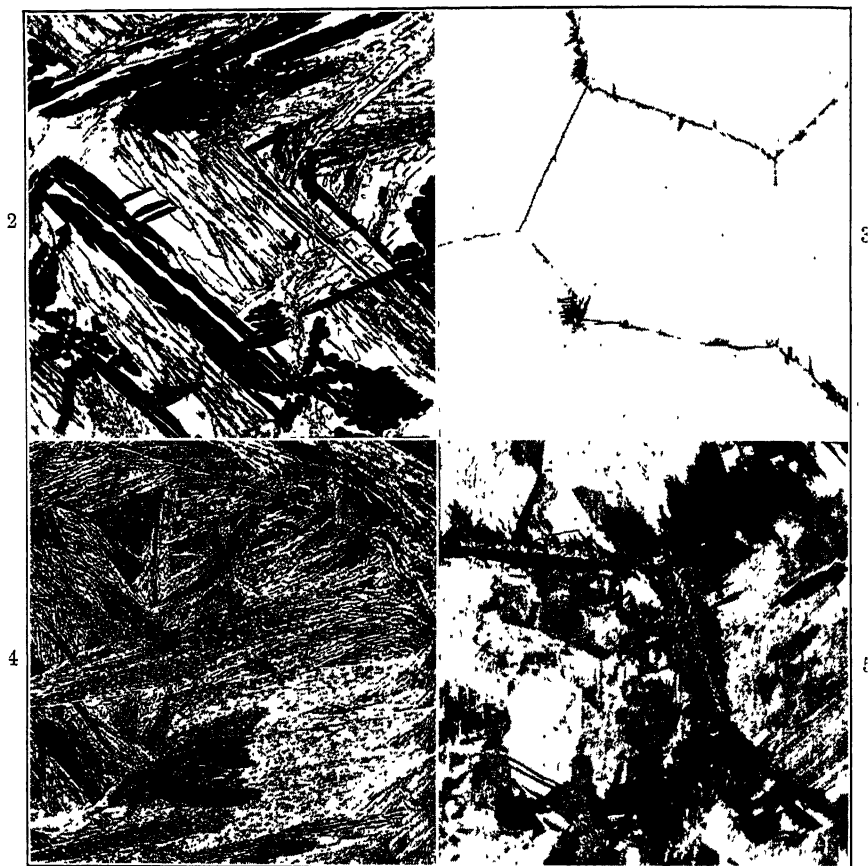
FIG. 2.—SPECIMEN AIR-COOLED FROM 850° C. × 75.
Composition: 60.30 per cent. Cu, 0.01 per cent. Pb, 0.01 per cent. Fe, 39.68 per cent. Zn (by difference).
FIG. 3.—SPECIMEN QUENCHED FROM 870° TO −8° C. × 75.
Composition: 60.30 per cent. Cu, 0.01 per cent. Pb, 0.01 per cent. Fe, 39.68 per cent. Zn (by difference).
FIG. 4.—SPECIMEN QUENCHED FROM 850° TO 20° C. × 75.
Composition: 62.10 per cent. Cu, 0.11 per cent. Pb, 0.01 per cent. Fe, 37.78 per cent. Zn (by difference).
FIG. 5.—SPECIMEN QUENCHED FROM 850° TO −11° C. × 75.
Composition: 62.10 per cent. Cu, 0.11 per cent. Pb, 0.01 per cent. Fe, 37.78 per cent. Zn (by difference).
All etched with 15 per cent. solution of dioxygen in concentrated NH_4OH.

illustrated by Fig. 2. Very rapid cooling of this alloy by quenching in water will not retain the beta structure, as with the 60/40 alloy, but yields a very fine alpha-beta structure as shown in Fig. 4. If a drastic

quench in brine maintained at $-10°$ C. be resorted to surprising results will be obtained. The structure will consist of large units outlined
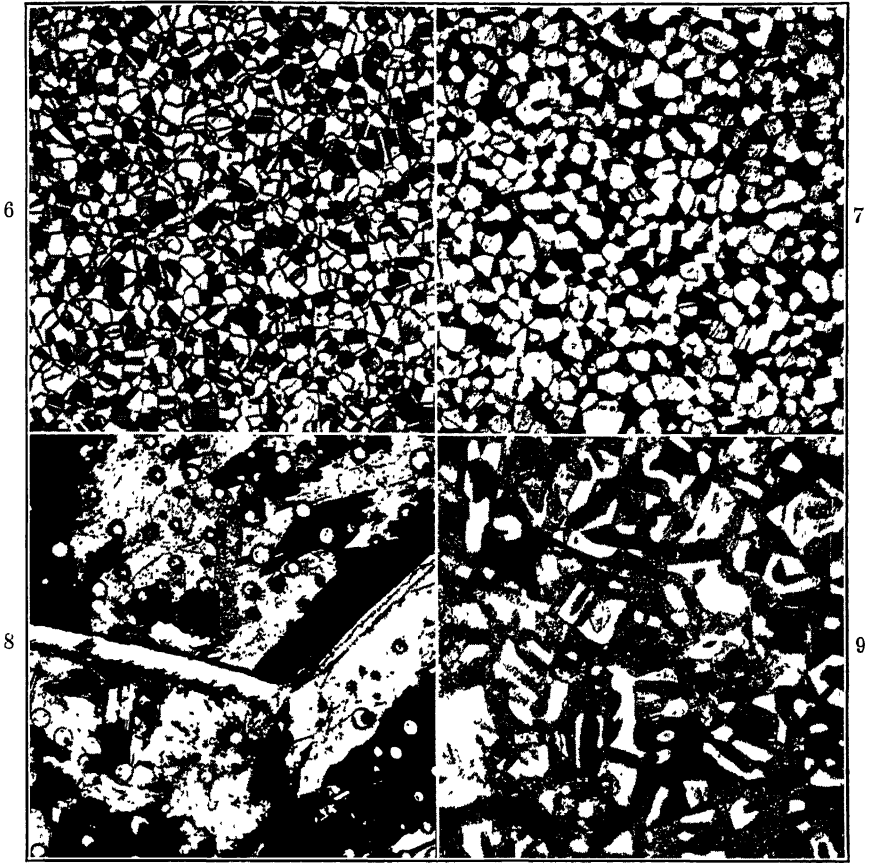
FIG. 6.—SPECIMEN QUENCHED FROM 750° TO 20° C. × 75.
Composition: 62.10 per cent. Cu, 0.11 per cent. Pb, 0.01 per cent. Fe, 37.78 per cent. Zn (by difference).
Etched with 15 per cent. solution of dioxygen in concentrated NH_4OH.
FIG. 7.—SAME SPECIMEN AS SHOWN IN FIG. 6 BUT ETCHED WITH FERRIC CHLORIDE TO DARKEN THE BETA AREAS.
FIG. 8.—SPECIMEN QUENCHED FROM 905° TO $-8°$ C. × 75.
Composition: 61.70 per cent. Cu, 0.06 per cent. Pb, 0.02 per cent. Fe, 38.22 per cent. Zn (by difference).
Etched with 15 per cent. solution of dioxygen in concentrated NH_4OH.
FIG. 9.—SPECIMEN QUENCHED FROM 900° TO $-13°$ C. × 75.
Composition: 63.03 per cent. Cu, 0.04 per cent. Pb, 0.02 per cent. Fe, 36.91 per cent. Zn (by difference).
Etched with 15 per cent. solution of dioxygen in concentrated NH_4OH.

with an alpha-beta fringe, *but the units instead of being beta will consist entirely of alpha.* This is illustrated by Fig. 5, in which the familiar alpha twins may be easily recognized.

Beta may be retained in this alloy with great ease if it is not heated to a temperature sufficient to convert the alpha into beta containing over 61 per cent. copper. In Figs. 6 and 7 the structure indicates that about half of the alloy is pure beta and yet the sample was merely water-quenched from 750° C. The alpha in the structure is essentially a residue of the original alpha in the sample prior to heat-treating. Superheating an alloy of 62 per cent. copper will also cause a retention of beta upon quenching. Fig. 8 shows a sample that was heated to incipient fusion and then quenched in ice brine at −8° C. The round spots and the grain boundaries were retained in the beta form while the rest of the alloy converted bodily into alpha.

Since the alpha structure produced upon quenching the 62 per cent. copper alloy from the beta range was quite unexpected, special means of insuring its identity were resorted to: (1) A specimen was etched with ferric chloride, a reagent which darkens beta but leaves alpha light. This treatment did not change the appearance of the large alpha areas but merely intensified the alpha-beta fringe at the crystal boundaries. (2) A polished and etched specimen was pinched in a vise producing slip lines characteristic of most metals crystallizing in the face-centered-cubic lattice. These slip lines showed the usual faultings through the twin bands present. Beta brass does not show slip lines upon slight cold working. (3) When a specimen was severely cold-worked it did not show the thin mechanical twin bands so easily produced in beta retained by quenching but deformed readily without cracking. (4) Upon annealing a specimen for 1 hr. at 550° C., there was no change in the appearance of the alpha. The alpha-beta fringe at the crystal boundaries, however, was converted entirely into alpha. This heat treatment brought about a decided drop in hardness which may have been due to the change at the crystal boundaries.

EXPERIMENTS ON A 63/37 BRASS

Brass containing 63 per cent. or more of copper cannot be converted entirely into the beta phase even at temperatures approaching the melting point. At 900° C. a specimen containing 63 per cent. copper will consist of slightly more than three-fourths beta and less than one-fourth residual alpha. If such a specimen is drastically quenched, the beta will not be retained as such nor will it be converted bodily into alpha but will break down by the precipitation of alpha just as a specimen of lower copper content will break down with a slower cooling rate (Fig. 4). This is illustrated by Fig. 9 which shows residual alpha surrounded by an alpha-beta matrix. If the specimen is not heated to a temperature exceeding 800° C., or if it is permitted to cool slowly to below that temperature before being quenched, little difficulty will be found in retaining

the beta at room temperature and the structure obtained will be very much like that shown in Fig. 6, but with proportionately less beta.

EXPLANATION OF RESULTS

The only unusual result obtained in the experiments just described is the production of an essentially alpha structure upon actively quenching an alloy of 62 per cent. copper from a temperature within the beta range (Fig. 5). This result may be explained by assuming that the transformation of beta into alpha, where no change in composition is concerned, can take place with great facility even at a rather low temperature. Consequently, if beta containing more than 61 per cent. copper, is cooled so rapidly through the alpha-beta range that the composition of the beta is not changed to less than 61 per cent. copper by the precipitation of alpha, then the beta can transform as a unit into alpha when it enters the alpha field.

If the cooling rate is too slow (Fig. 4), the separation of alpha in the alpha-beta range is permitted and consequently, the beta is lowered in copper content so that it can no longer be bodily converted into alpha. For this reason, under ordinary cooling conditions small amounts of beta are usually retained in alloys of about 61 per cent. copper since the absorption of beta through diffusion is exceedingly slow at low temperatures.

In the case of an alloy containing 60 per cent. copper (Figs. 2 and 3) beta cannot convert into alpha without a change in composition, and as this is necessarily accompanied by diffusion the process is relatively slow and the alloy is easily retained essentially in the beta form upon rapid cooling.

Even with alloys containing over 61 per cent. copper, beta is retained regardless of the quenching treatment if the temperature is so low that the beta constituent contains less than 61 per cent. copper. Thus, by heating such an alloy to 775° C. (Figs. 6 and 7) the beta contains only 60 per cent. copper and consequently will be retained as such upon quenching. In a similar fashion metal overheated so that it is partly melted (Fig. 8) is retained in the melted areas in the beta form upon quenching since these areas are lowered in composition to 60 per cent. copper.

In the light of the theory advanced the results obtained upon drastically quenching an alloy of 63 per cent. copper from 900° C. (Fig. 9) are rather unexpected. It is natural to expect that since the beta contains more than 61 per cent. copper it should convert bodily into alpha. Hence, the alloy should consist essentially of alpha in two forms; residual alpha containing about 67 per cent. copper and converted alpha containing 62.5 per cent. copper. Yet the fact remains that upon quenching, the beta breaks down by the precipitation of alpha, even with a very

rapid cooling rate, so that the structure eventually consists of residual alpha and precipitated alpha and beta.   There are two possible explanations for this result.   One is that the residual alpha areas in the alloy act as nuclei for the further precipitation of alpha on quenching so that it is impossible to retain a supersaturated beta solid solution.   Another explanation is based on the fact that the beta, since it is in contact with the alpha, is absolutely saturated at any temperature to which it is heated. Consequently, in the short, slow-cooling interval which elapses between withdrawing the specimen from the furnace and quenching in the freezing solution, alpha may start to separate.   Alloys not having residual alpha at the moment of quenching may be cooled in some cases as much as 75° C. before alpha will begin to precipitate.   Hence, there is ample time to remove the specimen from the furnace and place it in a quenching medium without the separation of alpha.

SUMMARY

Conversion from beta to alpha in brass takes place with very great rapidity if there is no change in composition.

ACKNOWLEDGMENTS

DISCUSSION

C H. MATHEWSON, New Haven, Conn.—There is one thing I would like to emphasize; namely, that in this day of critical revision of constitutional diagrams, we all of us must feel gratified to get information that gives us confidence in some of the diagrams as we already have them.   Certainly Dr. Phillips' contribution does that in one rather important respect.   If we look at the diagram in Fig. 1, we see that it represents the copper-zinc diagram in the currently accepted revised form.   The beta field in its upper left-hand corner lies over a part of the alpha field, representing saturation in zinc at low temperatures.   The course of the solubility curve bounding the alpha plus beta field on the left has been determined by the usual run of quenching and annealing experiments in which some novelties of treatment have been introduced by Genders and Bailey, and there is every reason to have confidence in the results, but I think anything in the way of direct confirmation such as Dr. Phillips has offered is very welcome.

What he shows in a very opportune little experiment is that beta can be transformed directly into alpha.   In other words, that there can be alpha and beta of the same ultimate composition.   That is precisely what the diagram indicates.   Any direct confirmation of this sort is of value in demonstrating the usefulness of a constitutional diagram.

There is one other point, concerning Fig. 9.   This represents an alloy containing 63 per cent. of copper, which shows a considerable quantity of coarse alpha.   This concentration is located almost exactly at the point where the beta boundary curves

intersect close to 900° C. in the upper right-hand part of the diagram. Thus, there should not be any coarse alpha to speak of in the quenched alloy.

I assume that Dr. Phillips has been very careful with his analytical work; that the composition is accurately given. The question then is whether there should not be some little modification of the dotted line in the diagram, separating the alpha plus beta from the beta field. In other words, whether it should not curve somewhat towards the right as it meets the peritectic horizontal so as to permit the presence of alpha and beta. If this does not happen, it may be possible that in heating up the alloy some of the alpha was not absorbed. However, I think this is rather improbable because in neighboring alloys there was no difficulty in absorbing the alpha, and the adjustment between alpha and beta apparently takes place very rapidly in this high-temperature region.

Another interpretation that might be offered is that this alloy was actually heated up into the melting zone, so that it consisted at the time of quenching of a mixture of liquid and alpha. This also appears improbable because of the character of the photomicrograph.

Perhaps the explanation that Dr. Phillips himself gave, to account for the failure of this alloy to transform directly into alpha on quenching, properly accounts for the large amount of coarse alpha visible after quenching. He considers that with some alpha present at the beginning of quenching and the rate of adjustment between alpha and beta so rapid at that elevated temperature, there is a separation of alpha practically all the time on cooling, no matter what the quenching rate. In other words, it is not possible to quench an alloy of that character fast enough to suppress in this very high-temperature region the instantaneous separation of some alpha, which may even coalesce into coarse grains.

F. H. CLARK, New York, N. Y.—I would like to ask Mr. Phillips if he has made any X-ray studies of the 62 per cent. copper alloy, and if he has, is there any way of explaining this change by the distortion of the copper lattice which would show up in X-ray studies?

E. E. THUM, New York, N. Y.—I would like to broaden Miss Clark's question somewhat. Perhaps I am only exhibiting my own ignorance in asking what is the essential difference between the alpha solid solution and the beta solid solution, but perhaps there are other people in this audience who have not followed the metallographical researchs as closely as they might have wished.

A. J. PHILLIPS.—Dr. Mathewson's explanation of Fig. 9 is logical. The fact that residual alpha does act as a nucleus upon which additional alpha can readily be precipitated, resulting in unexpectedly large areas of solid alpha, is also shown by Figs. 6 and 7. According to the diagram these photomicrographs should show less than 50 per cent. alpha, but Fig. 7 distinctly shows more than this amount in spite of the fact that the alpha must have been converted from beta containing less than 61 per cent. copper. Of course, it should also be remembered that the quenching temperatures given are probably several degrees higher than the actual temperatures of the specimens at the moment they entered the cooling medium because a special quenching furnace like that described by Dr. Rosenhain was not available.

In reply to Dr. Clark's question, no critical X-ray study has been made of the alloys because when preliminary powder photographs of the specimen illustrated by Fig. 3 were made it was found that instead of obtaining the lines characteristic of the body-centered cubic lattice (the atomic structure of beta brass) the lines characteristic of the face-centered cubic lattice (the atomic structure of alpha brass) were obtained. It was evident that the mechanical work upon the metal and the heat generated by filing converted the powder from the beta phase into the alpha phase. From the composition of the alloy and the equilibrium diagram, it is evident that there should

have been more than 10 per cent. beta present in the powder, yet the X-ray photographs showed no trace of the beta phase. When synthetic mixtures of alpha and beta powders were made up it was found that 10 per cent. of beta in alpha produced clearly recognizable lines in the spectrum. This probably indicates that the alpha/alpha-beta boundary cannot be extrapolated vertically to room temperature as is commonly done.

These preliminary experiments showed that X-ray studies using the convenient powder method would have to be postponed until a method has been devised of preparing powders that would represent the various specimens. Neither the pin-hole nor the Bragg type of X-ray spectroscopy was considered, because of the obvious difficulties of applying these methods to the specimens available.

Note on the Crystal Structure of the Alpha Copper-tin Alloys*

By Robert F. Mehl† and Charles S. Barrett,‡ Anacostia, D. C.

(Cleveland Meeting, September, 1929)

It is generally understood by workers in the field of the crystal structure of metallic alloys that terminal solid solutions are of two types, the substitutional and the interstitial. In reviewing the literature, the work of Weiss[1] on the crystal structure of the alpha copper-tin alloys was encountered, in which a new type of terminal solid solution was proposed. In brief, Weiss' findings showed that the density of the alloys calculated from the side of the unit face-centered cube on the assumption of simple substitution—that is, with four atoms to the unit face-centered cell—was much higher than the density measured directly. It was suggested that the assumption of four atoms to the unit cube is not valid for these alloys, and that each unit cube contained less than four atoms; in other words, that one tin atom replaces more than one copper atom, leaving some atomic positions unoccupied.

Such a structure, if verified, would have far-reaching significance in the study of the crystal structure of metallic alloys. It would indicate a complexity in terminal solid solutions not hitherto suspected and might encourage work leading to the discovery of other alloys of the same type, and perhaps to types intermediate between it and the two recognized types. It is of importance, therefore, to reinvestigate these alloys with respect to the type of solid-solution structure obtaining therein.

Materials and Experimental Method

The alloys were prepared from electrolytic copper cut directly from the cathode and the high-purity tin furnished by the U. S. Bureau of Standards for the calibration of thermocouples. No analyses for impurities of these materials or of the finished alloys were made, since such impurities as might be present could have only a wholly inappreciable effect upon the data obtained and the conclusions drawn. The alloys were made by melting the weighed copper charge in a graphite crucible under a KCl-LiCl flux with later additions of NaCl, using induction heating. When the copper was melted the weighed portions of tin were

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[1] H. Weiss: Application of X-rays to the Study of Alloys. *Proc. Roy. Soc.* [London] (1925) **108A**, 643.

introduced, the mix stirred thoroughly with a carbon rod and kept molten for about eight minutes. The alloy was then cast in a vertical steel mold, the sides of which were painted with a lime wash. This produced ingots 1 in. square in cross-section and 12 in. long.

Three alloys were made, of approximate compositions 4, 8, and 12 weight per cent. tin respectively. To insure homogeneity, both physical and chemical, the cast alloys were annealed 24 hr., the 4 per cent. alloy at 750° C. and the 8 and 12 per cent. at 700° C., then hammered cold to a 40 per cent. reduction in height, again annealed at the same temperatures for 24 hr. then again hammered cold to a 30 per cent. reduction in height, and again annealed for 30 hr. The finished alloys were examined under the metallurgical microscope after grinding a 1 to 2-mm. layer from the surface, and found to be without cracks or voids. An electrolytic determination of copper on the finished alloys gave the compositions noted in Table 1.

The side of the unit face-centered cube was determined by the use of the familiar General Electric Company's X-ray diffraction apparatus. The alloy was reduced to "powder" form by filing, and the powder obtained annealed *in vacuo* for $\frac{1}{2}$ hr. at the stated annealing temperatures to remove the strains produced by the filing operation. The alloy powder was packed in one half of a Pyrex tube 0.5-mm. inside diameter, and high-purity copper, prepared in the same way, was packed in the other half to serve the purpose of calibration. The side of the unit cube, a_o, of pure copper was taken as 3.603 Å. The best value of a_o for the alloys was obtained by the use of probability paper.

The densities of the alloys were measured on small pieces cut from the finished alloys. These pieces were thoroughly cleaned and dried by warming *in vacuo*. Their weight in air was determined after they had been allowed to remain 12 hr. in the balance case. To obtain their true weight in water they were boiled at room temperature in distilled water for $\frac{1}{2}$ hr. and weighed without removal from water, supported by a platinized platinum wire attached to the balance arm. The calculated densities were corrected for displacement of air, and refer to a temperature of 22° C.

RESULTS AND CONCLUSIONS

The data obtained for a_o and for the densities are given in Table 1 and diagrammatically in Figs. 1 and 2.

Besides Weiss' determinations of density and those given here, we have those by Maey[2] and by Norbury.[3] Norbury's densities were

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[2] Cited in Guertler's *Metallographie* (1924) **2**, *Das Volumen*, 41.

[3] A. L. Norbury: Volumes Occupied by the Solute Atoms in Certain Metallic Solid Solutions and Their Consequent Hardening Effects. *Trans.* Faraday Soc. (1924) **19**, 586.

determined with great care; each alloy was repeatedly hammered and annealed in a fashion similar to that carried out in the present work. The relation between the five sets of determinations available for comparison can be seen in Fig. 2.

TABLE 1.—*Side of Unit Cube and Density of Copper-tin Alloys*

Weight Per Cent Tin	Atomic Per Cent Tin	A_o		Density	
4.2	2.3	3.623 3.627	3.625	8.914 8.920	8.917
8.2	4.6	3.647 3.646 3.642	3.645	8.896 8.899	8.898
12.2	6.9	3.675 3.673	3.674	8.921 8.892	8.906

The values of a_o are plotted in Fig. 1. The results we have obtained agree very well with those of Weiss, and the single determination by Bain.[4]

It may be seen immediately from Fig. 2 that there is a serious difference between the densities determined in this work and those determined by Weiss. The present results are very closely in agreement with
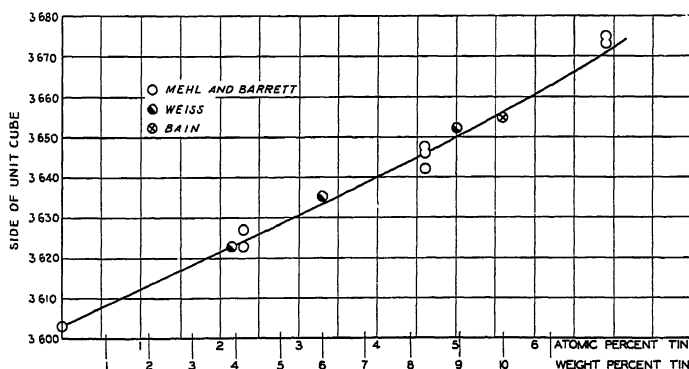
FIG. 1.

those of Norbury. It is to be noted that Weiss made his density measurements on alloys prepared by cooling the molten alloy to room temperature in the furnace, and, though he could not discover any voids upon microscopical inspection, the lower density values which he obtained are doubtless to be traced to an insufficient homogenization of the alloys

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[4] E. C. Bain: The Nature of Solid Solutions. *Chem. & Met. Eng.* (1923) **28**, 21.

studied.   Using the density figures obtained in the present work, or those of Norbury in a smaller concentration range, it may be seen that a close concordance is obtained with the theoretical densities as calculated from the assumption of simple substitution.   The observed densities are somewhat lower, but the difference is of the order of magnitude commonly experienced in making such comparisons even for pure metals.   It should be especially noted that the assumption of the substitution of a tin atom for two copper atoms, next to simple substitution the simplest
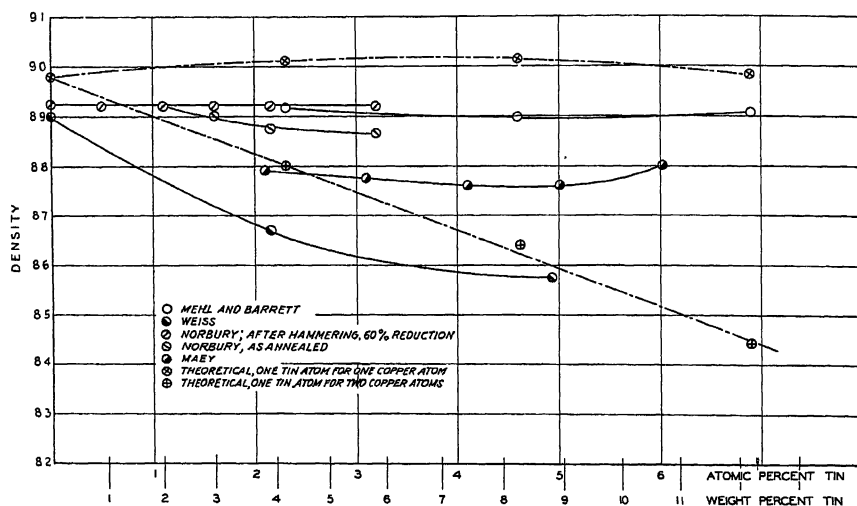
Fig. 2.

ratio, gives a density curve (Fig. 2) which diverges from the curve of simple substitution with increasing tin content.   No such divergence is apparent in the curve of directly determined densities.   It seems, therefore, that the alpha solid solution in the copper-tin system is merely another example of the substitutional type.

Summary

The side of the unit face-centered cube and the density were determined for three alloy compositions in the alpha field of the copper-tin system.   It is shown, contrary to previously published work, that this solid solution is simple substitutional in type.

The Eutectic Composition of Copper and Tin

By G. O. Hiers* and G. P. de Forest,* New York, N. Y.

The object of the experiments reported in this paper is to determine the eutectic composition of copper and tin and to determine the location of the part of the liquidus line immediately above the eutectic composition in copper. Three methods were used in the investigation: (1) the method of dissolving copper in a bath of molten tin at constant temperature, with the idea that when the bath was saturated with copper its copper content, by analysis, together with the temperature at which the saturation took place would locate a point on the liquidus line; (2) the method of the differential cooling curves, and (3) the method of microscopic examination. This paper is principally concerned with the results of the last two methods mentioned. The results of the first method, that of dissolving copper in molten tin, did not agree with the results of Miller,[1] by the same method, nor with the results of other investigators by other methods, nor yet with the results of the cooling-curve experiments and microscopic examination reported here.

Solution of Copper in Molten Tin

To determine the amount of copper that would be dissolved by molten tin at a given constant temperature the apparatus shown in Fig. 1 was used. It consists of a cast-iron pot a, 6 in. deep and 8 in. dia., well cleaned inside and dressed with graphite. This pot, which holds 15 lb. of tin, g, rests on a hot plate b with resistance winding c. The thermocouple d leads to a Wilson-Maeulen temperature regulator for maintaining the temperature at the heating coils at a fixed temperature to within $\pm 5°C$. There is a shallow bath of solder e on the top of the hot plate to improve the thermal contact between the plate and the pot. An insulating jacket f of asbestos prevents the irregular radiation of heat from the apparatus. The copper stirrer h slowly rotates in, and is dissolved by the bath of molten tin g. This bath is protected from excessive oxidation by a layer of charcoal j. The stirrer h is fixed to the lower end of the iron tube k, which is so mounted that it can be driven by a motor with reducing gear. The temperature of the bath is indicated

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[1] H. J. Miller: Penetration of Brass by Tin and Solder, with a few notes on the Copper-tin Equilibrium Diagram. *Jnl.* Inst. Met. (1927) **37**, 183.

by a potentiometer connected to the iron constantan thermocouple l, the lower end of which projects below the end of the tube k into the bath. By the hel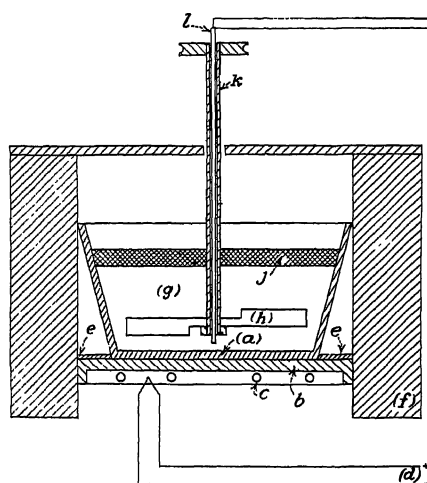p of the inertia of the hot plate, pot and bath, the maximum temperature variation of the bath at the junction of the thermocouple l was $\pm 2°$ C. and was usually within $\pm 1°$ C.

FIG. 1.—DISSOLUTION APPARATUS.

From time to time the stirrer was removed, the bath was thoroughly stirred with a ladle and a sample, $\frac{1}{8}$ in. thick, immediately cast in a cast-iron mold. The sample solidified in about 5 sec. Sawings of this sample were taken for analysis to determine the copper content. When analysis showed that the copper content remained sensibly constant in successive samples the experiment was stopped.

The results obtained from the experiment on the solution of copper in tin are at wide variance with those obtained by cooling-curve deter-
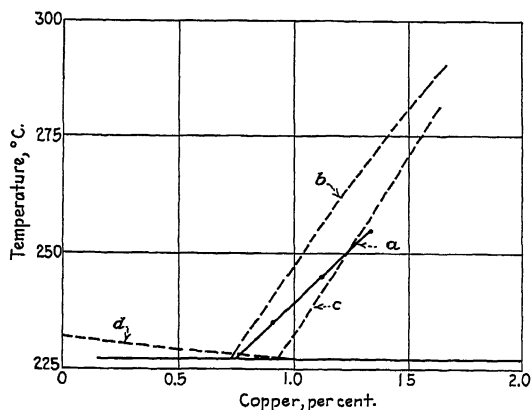
FIG. 2.—COMPARISON OF CURVES.

a. Liquidus line from dissolution experiments.
b. Liquidus line after Miller.
c. Liquidus line from cooling-curve experiments.
d. Liquidus line after Gurevich and Hromatko.

minations and microscopic examination. Although these results are in better agreement with those of Miller, curve b Fig. 2, than with any other they have serious weaknesses which render their value doubtful.

The entire value of such experiments depends on a very close approach to equilibrium. To insure this equilibrium the bath in which the copper is being dissolved must be at a constant and uniform temperature and the dissolved copper must be uniformly diffused throughout the bath. Now suppose that the whole bath is nearly saturated with copper and that a small drop in temperature takes place in one part of the bath. Some epsilon solid solution will form with a liberation of heat. Theoretically this liberation of heat should melt the epsilon crystals and restore the bath to equilibrium but actually it is possible that more copper may be dissolved from the stirrer. If excess copper is dissolved, it will remain in the bath as suspended epsilon crystals and the bath will have a higher copper content than that required for equilibrium. It is well to note that the surface of the stirrer is always coated with copper-tin alloy, evidently epsilon solid solution, which is dissolved by the tin bath.

TABLE 1.—*Solution of Copper in Molten Tin*

Constant Temperature, Deg. C.	Time of Exposure of Copper to Tin Bath, Hours	Copper Dissolved, Per Cent.	Indicated Limit of Solubility, Per Cent. Cu
235	1.5	0 65	
	6.0	0.68	
	10.0	0.88	
	13.0	0.91	0.91
245	16.0	1.06	
	20.0	1.07	
	23.0	1.07	
	39.0	1.12	1.12
255	6.6	1.22	
	22.0	1.31	
	68.5	1.33	1.33

This might account for the point, curve *a* Fig. 2, at 255° C. which has a higher copper content for the temperature indicated than that shown by the liquidus line, curve *c*, obtained from the cooling curves. The disagreement of the points shown on curve *a* at 245° C. and 235° C. with the corresponding points on curve *c* can not, of course, be explained in this way, but it is probable that the experiments from which these points were obtained were not continued long enough for the bath to be saturated with copper (Table 1). In view of these considerations it is not felt that the evidence obtained from the solution experiments should receive as much weight as that from the cooling curves and microscopic examination.

DIFFERENTIAL COOLING CURVES

The differential cooling-curve apparatus used in this investigation is shown in Fig. 3. The apparatus consists of a neutral body a of silver weighing 300 g. It is $2\frac{1}{2}$ in. long, 1 in. dia. and has a shallow $\frac{3}{8}$-in. hole drilled longitudinally. The top of this hole is tapped and fitted with a plug s of the same material. This hole contains a small conical sheet-iron cup, 0.02 in. thick and weighing 0.3 g., to the apex of which are welded four wires, B. & S. gage 22, two of iron and two of constantan. One pair of these wires (one iron and one constantan), m and n, is led to a potentiometer p. Of the other pair, the iron one l is led to the reflecting galvanometer G; the other, j, of constantan is led to the point t, where it is welded to the iron wire k, which is then led to the other terminal of the galvanometer G. The neutral body a is surrounded by an alundum tube d which is wound with resistance wire e. This tube is surrounded by the hollow sheet-iron drum f and the ends of the tube are plugged with asbestos h. This drum is surrounded by a larger sheet-iron drum g.
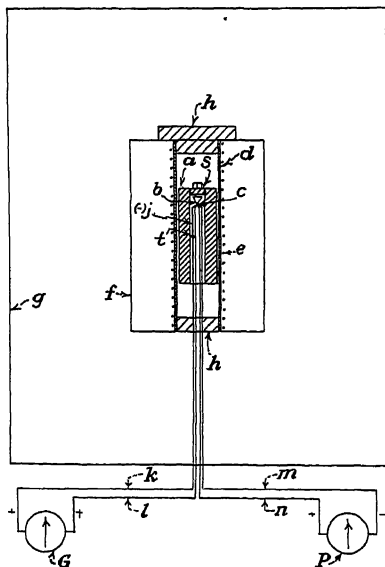
FIG. 3.—COOLING-CURVE APPARATUS.

The cup b, which is coated inside with a little graphite, holds the sample of which the cooling curve is to be determined. The apparatus is operated as an ordinary differential cooling-curve apparatus. Potentiometer P indicates the temperature at point c and the galvanometer G indicates any change in the difference in temperature between the points t and c; i. e., between the neutral body and the cup. Point t is sensibly at the temperature of the neutral body and point c is sensibly at the temperature of the sample. Any constant lag that exists is corrected for in the calibration of the apparatus.

Stock from which the cooling-curve samples were taken was made as follows: A base alloy of 9.16 per cent. copper was made under a reducing atmosphere by dissolving electrolytic copper of over 99.93 per cent. purity in tin of the following composition: copper, 0.0038 per cent.; iron, 0.0016; antimony, not more than a trace; bismuth, not more than a trace; arsenic, not more than a trace; zinc, not more than a trace; tin, 99.9946 (by difference). This base alloy was diluted with tin under a reducing atmosphere to give alloys of the following composition by

analysis: 0.20, 0.40, 0.70, 0.82, 0.95, 1.04, 1.22, 1.42, and 1.66 per cent. copper.

From a melt of 500 g. of each alloy, a 225-g. casting was poured in a cast-iron, water-cooled mold. The melt was thoroughly stirred immediately before pouring and the castings solidified in less than 15 sec. Sawings were made from each of these castings. The sawings
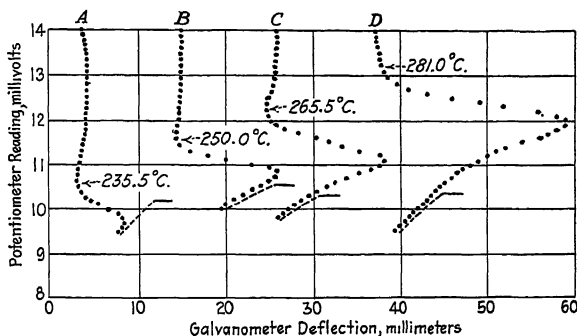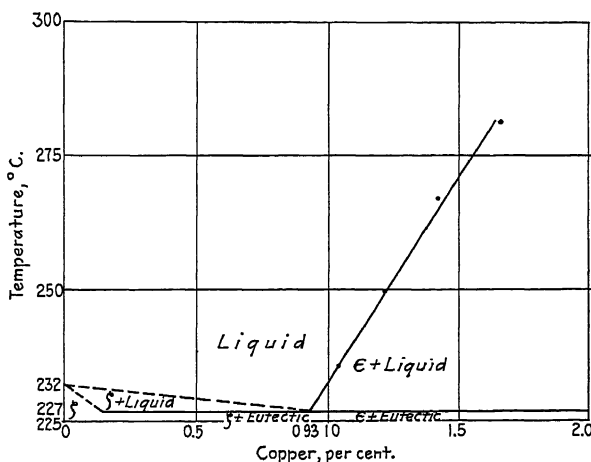

FIG. 4.—TYPICAL COOLING CURVES.

FIG. 5.—EQUILIBRIUM DIAGRAM FROM COOLING CURVES.

from each casting were thoroughly mixed, part being taken for the cooling-curve samples and part for analysis. Of the part taken for the cooling-curve samples three buttons were made of 0.500 g. each, by melting the sawings under rosin in a mold identical to the cup b (Fig. 3). Of each of these buttons three cooling curves were made as follows:

The ½-g. sample to be used, after being thoroughly cleaned with ether, was put into the cup b of the cooling-curve apparatus (Fig. 3). The plug s was screwed into place; the asbestos plug h was put into the top of the cylinder d and the top of the drum g was closed.

The resistance winding e was energized. When the temperature of the cup, as indicated by the potentiometer P, was about 60° C. above the recalescence temperature, the heating coil was de-energized and the apparatus allowed to cool at the rate of about 12° C. per minute. As the neutral body a and cup b, containing the sample cooled, a reading was taken on the galvanometer G for every 0.1-mv. (2° C.) change in the reading of the potentiometer. The recalescence temperature was determined from the plot of the galvanometer readings as a function of the potentiometer readings (Fig. 4).

TABLE 2.—*Cooling-curve Data—Temperature of Recalescence*

Sample	Alloy 1E6 1.04 Per Cent. Cu.	Alloy 1E7 1.22 Per Cent. Cu.	Alloy 1E8 1 42 Per Cent. Cu.	Alloy 1E9 1 66 Per Cent Cu
	Deg. C.	Deg. C.	Deg. C.	Deg C.
a	235 5	244.0	261 0	281 0
	231 0	247 0	269 5	278 5
	233 0	247 0	273 5	280.5
Average..	233.0	246.0	268.0	280.0
b.............	241.0	246 0	265.0	288 0
	235 0	246 0	271 5	287.0
	236.0	255 5	267 5	285.0
Average.	237.5	249 0	268.0	287.0
c.........	231.5	250.0	265.5	274.0
	235 0	254.0	266.5	278.0
	240.0	255.0	265 0	282 0
Average.	235 5	253.0	265 5	278.0
Mean............	235.5	249.5	267.0	281.5
Ind. avg. dev	2.5	3.8	2 9	3.9
Mean avg. dev.	0.83	1.3	0 93	1 3
Probable error..	0 74	1.2	0 88	1.2

The recalescence temperatures so obtained are given in Table 2, together with their mean values. These mean values are plotted in Fig. 5 and through them is drawn a mean straight line which intersects the horizontal at the eutectic temperature (227.1° C.)[2] at 0.93 per cent. copper.

MICROSCOPIC EXAMINATION

From each of the chill castings described a sample about $\frac{3}{8}$ in. square and $\frac{1}{4}$ in. thick was cut for microscopic examination. Another

[2] L. J. Gurevich and J. S. Hromatko: Tin Fusible Boiler-plug Manufacture and Testing. *Trans.* A. I. M. E. (1920) **64**, 227.

set of slowly cooled castings was prepared for microscopic examination. For each casting 400 g. of alloy were melted in a graphite crucible to 300° C., stirred and allowed to cool slowly in surroundings at a temperature of 150° C. Each casting was then machined as shown in Fig. 6. Part a was wasted; part b, as turnings, was sampled and analyzed; part c was prepared for microscopic examination and the surface d was polished. The castings as analyzed showed respectively the following copper contents: 0.22, 0.33, 0.67, 0.91, 1.28, 1.50, and 1.53 per cent.

In preparing the specimens for microscopic examination the following procedure was observed:

The face of the casting d from which the sample was to be cut was carefully machined in a lathe at a speed of 400 r.p.m. with a cross feed of 0.0045 in. per revolution with a round-nosed tool of large clearances and a sharp smooth cutting edge. A sample c was carefully sawed from the casting and the machined surface d polished on Manning emery papers from No. 0 to No. 000 with a medium of paraffin dissolved in kerosene. After an operation was completed on each polishing paper the sample was etched with 10 or 20 per cent. hydrochloric acid as required, for 2 to 3 min., to remove any metal that might have been flowed on the polished surface. After the polishing on the No. 000 paper, and etching, the sample was polished on a polishing wheel covered with the best grade of broadcloth. For a polishing medium a solution of soap and levigated alundum grain was used. When all the scratches caused by the paper had been removed the sample was etched as before and polished on a second wheel covered with a high grade of silk velvet, using the same polishing medium as for the broadcloth. The specimen was alternately polished on this wheel and etched until the structure was satisfactorily developed.

FIG. 6.—METHOD OF MACHINING CASTINGS.

This method was fairly rapid, produced a surface fairly free from scratches, eliminated flowed metal on the polished surface, and satisfactorily developed the structure without pitting. All the etching reagents containing nitric or acetic acid that were tried produced pitting, and etching reagents not containing these reagents, with the exception of the hydrochloric acid reagent mentioned above, did not satisfactorily develop the structure.

FIGS. 7–12.—CAPTIONS ON OPPOSITE PAGE.

The solution of paraffin and kerosene was prepared by dissolving 100 g. of paraffin in 200 c.c. of warm kerosene. The mixture was used warm because at room temperature it is almost solid.

The solution of soap and levigated alundum grain was prepared as follows: 5 g. of alundum grain (Norton size 600 grain No. 25925) were added to 300 c.c. of water. This mixture was thoroughly agitated and allowed to stand for 15 min., when the supernatant suspension was decanted. To this decanted suspension 40 g. of soap were added and the mixture heated until the soap was dissolved. This mixture is also nearly solid at room temperature, so that it is necessary to use it warm. When this polishing medium was poured on to the polishing wheel it formed a gelatinous mass, viscous enough so that it was not thrown off the wheel which was driven at 120 r.p.m.

To remove the paraffin before etching, the samples were washed in warm kerosene and the kerosene was removed by washing the specimen between the palms of the hands with soap and water. To remove the soap the samples were held in a strong stream of warm water for about one minute. If these precautions were not observed the etching was likely to be uneven. Finer abrasives than the alundum grain were tried but although these gave a polished surface more free from scratches a burnishing action and relief polishing were almost sure to follow.

DISCUSSION OF RESULTS

In the consideration of the results on the determination of the eutectic composition of the copper-tin system it is important to remember that equilibrium is difficult to attain. It follows that the more independent a method is of equilibrium the more reliable that method should be. To obtain equilibrium by slow cooling in an alloy of hypereutectic or hypo-eutectic composition the cooling must be so slow that the solidifying primary constituent will have time to come to equilibrium with the liquid at a temperature immediately above that of the eutectic. At the eutectic composition, however, since there is no constituent in excess, the only thing that can occur is the formation of the eutectic regardless of whether the cooling rate is fast or slow. Portevin[3] shows, from theoretical considerations, that where only one constituent surfuses, the eutectic mixture resulting from the solidification of a liquid of true eutectic composition may show an excess of that constituent which

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[3] A. M. Portevin: The Structure of Eutectics. *Jnl.* Inst. Met. (1923) **29**, 239.

FIG. 7.—0.67 PER CENT. Cu, SLOWLY COOLED. × 100.
FIG. 8.—0.82 PER CENT. Cu, CHILL CAST. × 100.
FIG. 9.—0.91 PER CENT. Cu, SLOWLY COOLED. × 100.
FIG. 10.—0.95 PER CENT. Cu, CHILL CAST. × 100.
FIG. 11.—0.95 PER CENT. Cu, CHILL CAST. × 500.
FIG. 12.—1.04 PER CENT. Cu, CHILL CAST. × 100.

does not surfuse, but from the results of Rosenhain and Tucker[4] and of Brady[5] it seems probable that if such a condition exists it manifests itself in a variation in the composition within the eutectic grains but does not result in the appearance of primary crystals.

Therefore in determining the eutectic composition by microscopic examination if any primary constituent be observed the sample must be either hypoeutectic or hypereutectic. Neither need such a primary constituent be in equilibrium with the other constituents, as its mere presence is the criterion.

In the use of the cooling curves, since the eutectic temperature is known, equilibrium below the liquidus line is not significant. Lack of equilibrium as the specimen approaches the liquidus line during cooling evidently is important.

In general, the most serious source of error in determining the recalescence point seems to be temperature differences throughout the sample.[6] There is little probability of any serious difference in temperature between any two points in so small a globule of alloy (0.500 g.) as that used for the cooling curves in this investigation.

As mentioned, the intersection of the liquidus line, as constructed from the cooling-curve data, with the solidus line indicates a eutectic composition of 0.93 per cent. copper. This result is well supported by the microscopic examination, which indicates a eutectic composition of 0.95 per cent. copper. Fig. 10 shows a chill casting of 0.95 per cent. copper. The grains of fine eutectic and the grain boundaries show clearly with no appearance of zeta solid solution[7] or crystals of epsilon solid solution in excess of the eutectic structure. Fig. 11 is a photomicrograph of the same sample at a higher magnification, showing in more detail how completely the sample is composed of fine eutectic. Fig. 9 shows a slowly cooled sample with 0.91 per cent. copper. A slight excess of free zeta is seen at the grain boundaries, indicating that it is just below the eutectic composition (in copper content). By comparison, Fig. 8, of a chill-cast sample of 0.82 per cent. copper shows a large amount of free zeta. The zeta is the light, dendritic lace work; the eutectic is the dark groundmass. Fig. 7 (0.67 per cent. Cu, slowly cooled) also clearly shows a large amount of free zeta.

[4] W. Rosenhain and P. A. Tucker: Eutectic Research—No. 1. The Alloys of Lead and Tin. *Phil. Trans.* (1908) **209A**, 89.

[5] F. L. Brady: The Structure of Eutectics. *Jnl.* Inst. Met. (1922) **28**, 369.

[6] C. Benedicks: Metallographic Researches. New York, 1926. McGraw-Hill Book Co.

[7] The notation used here is that used by J. L. Haughton [Constitution of the Alloys of Copper with Tin. *Jnl.* Inst. Met. (1915) **13**, 222; *ibid.* (1921) **25**, 309] and in the A. S. S. T. data sheet for the copper-tin equilibrium diagram [W. A. Cowan, G. O. Hiers and F. H. Edwards: Handbook Amer. Soc. Steel Treating (1928) Sn-1219.].

Above the eutectic composition one would expect to see crystals of free epsilon. These are shown in Fig. 12 (1.04 per cent. Cu, chill cast) as small hollow needles surrounded by dendritic areas of free zeta (white). The areas of free zeta are apparently the solidified mass of liquid from which the copper to form the crystals was taken during the process of solidification. Because there was insufficient time they were not able to come to equilibrium with the surrounding mass. The dark ground area shows grains of eutectic. Fig. 13 is the same sample at 500 dia. and shows in more detail the appearance of the epsilon crystals surrounded by zeta and the groundmass of fine eutectic. Fig. 14, of still higher copper content (1.28 per cent.), shows the growth of the epsilon crystals with slow cooling. In such a sample it is difficult to distinguish large crystals of epsilon from coarse eutectic (crystals much larger than any seen in the photomicrograph were visible in the sample). Nevertheless the structure is in clear contrast with the hypoeutectic structure as shown

13   14
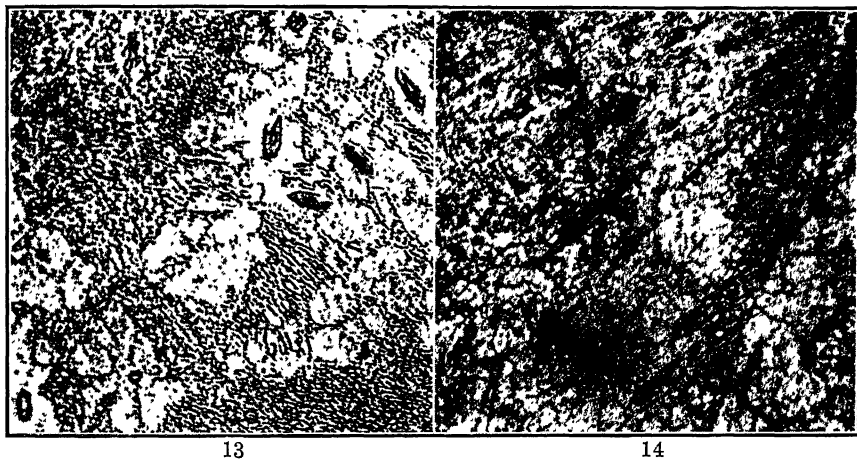
FIG. 13.—1.04 PER CENT. Cu, CHILL CAST. × 500.
FIG. 14.—1.28 PER CENT. Cu, SLOWLY COOLED. × 100.

in Figs. 7, 8, and 9. Neither tin oxide nor copper oxide was discovered in any of the microstructures.

From the evidence of the microscopic examination and the equilibrium diagram constructed on the cooling-curve data the most probable composition of the copper-tin eutectic is placed at 0.94 per cent. copper. This result is in good agreement with the conclusions of Gurevich and Hromatko[8] as well as with those of Heycock and Neville[9] who place the

[8] L. J. Gurevich and J. S. Hromatko: *op. cit.*

[9] C. T. Heycock and F. H. Neville: Constitution of the Copper-tin Series of Alloys. *Phil. Trans.* (1904) **202A**, 1.

eutectic composition at 1 per cent. copper.   The curve of the liquidus line between pure tin and the eutectic composition as given by Gurevich and Hromatko is shown as curve *d,* Fig. 2.

DISCUSSION

S. L. HOYT, Schenectady, N. Y.—Here, again, we have an attempt to correct or confirm previous constitution diagrams, and while the results have not given a new type of diagram, they undoubtedly constitute an advance or an improvement in this particular diagram.

It occurred to me, in reading over this paper, that the particular problem here would not be easy to solve on account of the supercooling effects of tin.   That would apply both to the microscopic method and to the thermal method, and I noticed in particular that the alloy, which is said to be the eutectic composition, was chill-cast.

Might not the copper oxide contained in the copper vitiate some of the results to some extent too, on account of the reaction between the tin and the copper oxide? That may have some bearing on the data obtained by dissolution.

How has the author taken these points into consideration?

G. O. HIERS.—We did our utmost to prevent oxidation, and we found no evidence of tin oxide in any of our microstructure studies.   Of course, we are not positive that there is no oxide present, but from our work with other alloys and actual determinations of oxygen in them, we are inclined to believe that that is practically insignificant in this case, although it is indirect evidence.

S. L. HOYT.—In regard to these impurities, I understood Mr. Hiers to point out in one of his photographs, epsilon surrounded by zeta, which in turn was surrounded by the eutectic.   In view of the eutectiferous diagram suggested here, the microscopic evidence is conflicting with the diagram proposed.   In other words, from this diagram you would not expect epsilon to be surrounded by zeta, which would in turn be surrounded by eutectic.   That is one of the main reasons why I brought up this point of impurities and the reaction between copper oxide and tin.

G. O. HIERS AND G. P. DE FOREST.—None of the samples shown in the photomicrographs are in perfect equilibrium.   It is not only from the proportions of the constituents in the samples, however, that conclusions as to the eutectic composition are drawn but from the presence or absence of any primary constituent.   This is admittedly not an absolutely precise indication in alloys that surfuse, as Portevin has shown, but the error is probably small.

That the pro-eutectic constituent, in a system forming a true eutectic, can exist surrounded by the other constituent, which in turn is surrounded by eutectic, is explained at the top of page 217.   This explanation is supported by Portevin.[10]   The assumed presence of impurities is not necessary to explain this phenomenon.

The possible presence and disturbing effect of copper oxide in the dissolution method is a sound assumption and increases the unreliability of that method.

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[10] A. M. Portevin: *Op. cit.,* 263.

Corrosion of Alloys Subjected to the Action of Locomotive Smoke

By F. L. Wolf,* Mansfield, Ohio

THE catenary system of line construction possesses so many desirable characteristics from the operating standpoint that it has wide application for all types of electric traction. Many steam roads are electrifying sections of their lines, and in most cases are operating both steam and electric locomotives over the same track. This means that the overhead catenary system is subjected to the severe corrosive action of locomotive smoke, and data concerning the resistance of various alloys to this form of corrosion are very desirable from every point of view. Reliable and specific information and data on the subject of corrosion due to steam and smoke from locomotives are extremely meager and, on this account, extensive service tests, together with accelerated tests, have been made on a number of commercial metals and alloys.

The observations and data recorded in this paper are the result of a preliminary test which was started in 1923 and which has been carried on to the present time. The recognition of the need for even more detailed and accurate data has resulted in the undertaking of another test which has been in progress for about a year. The result of this test will be published in due course.

Some years ago The Ohio Brass Co. was asked by one of the large steam railroad companies to furnish data on construction details for a catenary system which it was considering for one of its divisions. The selection of materials which would give the necessary physical characteristics as well as withstand the severe corrosive action of locomotive gases caused electrical railroad engineers considerable concern. At that time, there were available no specific or authentic data on these important questions: no systematic investigation of the problem appeared to have been made, even though its importance was generally recognized. Such observations as had been made were crude in that they had been limited largely to visual inspection which too frequently is most misleading. However, the scattered information which was collected gave important clues as to how best to start an investigation.

Technical literature was studied, metallurgical experts were consulted, and the problem was discussed with engineers who were in close contact

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* Chief Engineer and Technical Superintendent, The Ohio Brass Co.

with this and similar problems in the field, in an endeavor to obtain reliable data. The suggestions made and information obtained were of great assistance in subsequent investigations of the subject.

Sidney Withington, chief electrical engineer, and Harry F. Brown, assistant electrical engineer, of the New York, New Haven and Hartford R. R., had used, with considerable success, the smoke jack of the locomotive roundhouse as a test ground for making an accelerated test. They found that material suspended in the smoke jack and subjected to the concentrated action of locomotive smoke in a short time gave them a measure as to what could be expected of any material under actual service conditions. Since the need for accurate data was very pressing, it was decided to start an investigation at once, using as test materials those alloys which had already been used by the railroads and which apparently had given the required service. The alloys selected, while small in number, covered a fair range as to composition, and it was felt that a test on these would be indicative, if not conclusive.

The vast amount of information which is available on the subject of corrosion in general did not prove to be of great assistance on this specific problem. However, there were included in this test some of the outstanding examples of alloys which had been investigated previously, and in connection with a different form of corrosion. Among such alloys were manganese bronze, aluminum bronze, Muntz metal, Tobin bronze, and others. In order to make these tests more reliable, it was felt desirable to run simultaneous tests under actual service conditions in conjunction with the accelerated test plan.

The actual mechanism of the corrosion caused by locomotive smoke has not yet been definitely determined. However, in the products of combustion of coal there are found various amounts of sulfur dioxide. This, together with the water vapor present in the exhaust, produces sulfurous acid and eventually, in the presence of oxygen, sulfuric acid. The soot and tarry matter produced by the incomplete combustion of the coal is deposited on the overhead materials and there acts detrimentally as a retaining medium for the corrosive electrolyte and in itself composes one of the electrodes for the subsequent electrolysis which is set up, so that the electrolytic potential of the alloys tested against the soot which is deposited appears to be of extreme importance. However, this phase of the problem remains for further investigation.

Tests

Cast and stamped catenary clips were chosen for both the service and the accelerated tests. In addition, standard Izod impact bars were chosen for the accelerated test only. Test specimens were put into service on the New York, New Haven and Hartford R. R. just north of the

station at New Haven, Conn., and a duplicate set of test specimens were placed on the line at the west approach of the Hoosac Tunnel on the Boston and Maine R. R. near North Adams, Mass. The test specimens for the accelerated test were suspended in the smoke jack of the round-house of the Pennsylvania R. R. at Mansfield, Ohio, where for nearly 24 hr. each day they were subjected to the exhaust gases from large loco-motives. In all cases the stacks had no hoods and were open to the
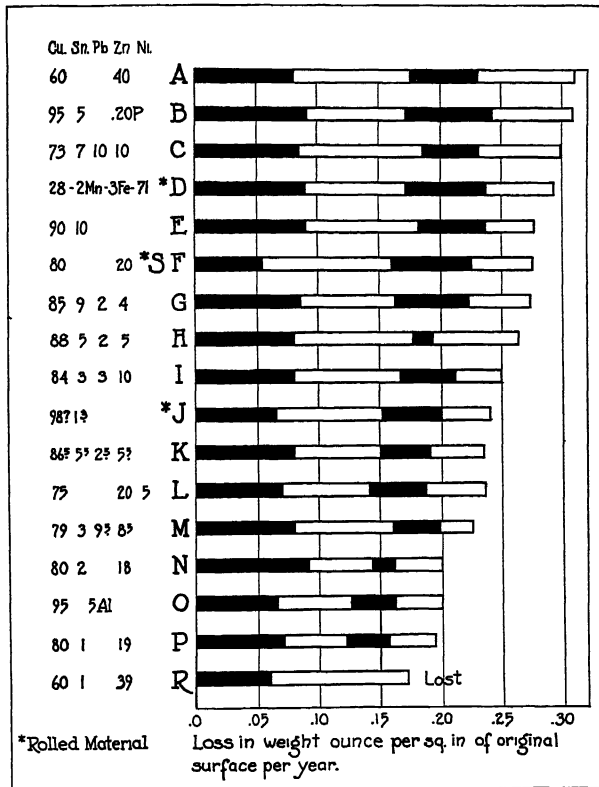

FIG. 1.—LOSSES OF VARIOUS ALLOYS EXPOSED IN SMOKE JACK FOR FOUR YEARS.

atmosphere. To simplify the identification of the individual test speci-mens, the code number of the alloy and the test piece number were marked with small drill holes and center punch marks.

One set of specimens of each alloy in the service test was removed from the overhead at approximately 6-month intervals, cleaned of soot and scale, inspected, and the loss in weight calculated in ounces per square inch of the original surface exposed. The accelerated test was run in two ways. In the first case, the specimens were removed each month, cleaned of soot and scale, inspected, and the loss in weight calcu-

lated in ounces per square inch of the original surface exposed. In the second case the specimens were not disturbed for a period of 48 months, at which time they were removed, cleaned of soot and scale, inspected, and the loss in weight calculated in ounces per square inch of the original surface exposed.

OBSERVATIONS

At the end of 48 months' exposure, it was necessary to discontinue the accelerated test. In too many cases the samples were so badly corroded that it was feared they would disappear entirely and thus entail a loss of much valuable data.

TABLE 1.—*Composition of Alloys Tested*

Code No.	Name	Chemical Composition				
		Copper, Per Cent.	Tin, Per Cent.	Lead, Per Cent.	Zinc, Per Cent.	
A	Muntz, cast..................	60.00			40.0	
B	Phosphorus bronze....	95.00	5.00			0 20 P
C	Red brass.............	79.00	1.00	10.00	10.0	
D	Copper-nickel...............	31.00				2.00 Mn 61.00 Ni
E	Tin bronze............	90.00	10.00			
F	Low brass..................	80.00			20.0	
G	Red brass..................	85.00	8.75	2.25	4.0	
H	Red brass..................	87.75	5.50	1.75	5.0	
I	Red brass................. .	84.00	3.00	3.00	10.0	
J	Copper alloy rolled....... ...	98.75	1.25			
K	Red brass...........	86.50	5.50	2.50	5.5	
L	Nickel brass............... .	75.00			20.0	5.00 Ni
M	Red brass..................	79.00	3.00	9.50	8.5	
N	Tinned low brass...	80.00	2.00		18.0	
O	Aluminum bronze......... ..	95 00				5.00 Al
P	Tinned low brass............	80.00	1.00		19.0	
Q	Manganese bronze..........	59.00			40.0	0.05 Mn
R	Tobin bronze......	60.00	1.00		3 9.0	
S	Low brass rolled.............	80.00			20.0	
T	Aluminum..................		99.8 aluminum			
U	Aluminum No. 12............	8.00	92 aluminum			

Table 1 lists the alloys tested in both the service and accelerated tests, together with their chemical compositions.

Table 2 shows the losses in ounces per square inch of original surface of the various nonferrous alloys in the form of Izod impact bars which were subjected to the accelerated test for a period of 4 years.

TABLE 2.—*Loss on Impact Bars after Exposure in Smoke Jack*

Ounces per Square Inch

Months	4	8	12	16	20	24	28	32	36	42	44	48
Alloy												
A	0.02	0.04	0.071	0.11	0.13	0.174	0.187	0.209	0.225	0.243	0.25	0.31
B	0.03	0.045	0.065	0.09	0.115	0.155	0.185	0.195	0.215	0.245	0.25	0.27
C	0.035	0.051	0.083	0.12	0.143	0.187	0.193	0.205	0.218	0.24	0.265	0.30
D	0.042	0 064	0.091	0.133	0.151	0.169	0.199	0.217	0.241	0.243	0.257	0.302
E	0.036	0.055	0.09	0.141	0.155	0.197	0.20	0.214	0.235	0.253	0.267	0.275
F	0.027	0.035	0.063	0.092	0.132	0.16	0.195	0.195	0.227	0.236	0.244	0.253
G	−0	0.049	0.14	0.15	0.145	0.171	0.183	0.203	0.216	0.231	0.248	0.29
H	0.033	0.047	0.081	0 125	0.130	0.192	0.171	0.18	0.191	0.211	0.221	0.28
I	0.03	0.043	0.073	0.11	0.136	0.163	0.172	0.188	0.209	0.210	0.223	0.26
J	0.03	0.043	0.07	0.108	0.12	0.151	0.164	0.191	0.20	0.211	0.22	
K	0 025	0.04	0.065	0.10	0.12	0.15	0.155	0.165	0.18	0.20	0.207	0.225
L	0.024	0.038	0.063	0 089	0.107	0.157	0.15	0.165	0.179	0.19	0.211	0.245
M	0.036	0 05	0.081	0.108	0.146	0.159	0.171	0.186	0.195	0.204	0.218	
N	0.036	0.062	0.093	0.106	0.118	0.143	0.135	0.172				
O	0.02	0.038	0.062	0.09	0.121	0.126	0.129	0.14	0.154	0.152	0.175	0.211
P	0.028	0.043	0.071	0.112	0.11	0.13	0.11	0.13	0.14	0.145	0.144	0.19
R	0.024	0.048	0.069	0.13	0.17	0.145	0.172	0.178	0.19	0.195	0.288	

Table 3 shows the losses in ounces per square inch of the original surface of the various nonferrous alloys in the form of catenary clips which were subjected to the accelerated test for a period of 2 years.

TABLE 3.—*Losses on Catenary Clips Exposed in Smoke Jack*

Ounces per Square Inch

Months	2	4	6	8	10	12	14	16	18	20	22	24
Alloy												
A	Failed											
B	0.008	0.017	0.046	0.051	0.071	0.085	0.096	0.11	0.118	0.137	0.154	
C	0.015	0.029	0.04	0.053	0.07	0.095	0.103	0.123	0.132	0.149	0.163	0.185
E	0.013	0.026	0.045	0.063	0.083	0.095	0.108	0.121	0.136	0.156	0.171	0.179
F	0.001	0.021	0.034	0.044	0.06	0.076	0.096	0.108	0.12	0.137	0.149	0.163
G	0.014	0.024	0.037	0.048	0.065	0.084	0.102	0.116	0.125	0.14	0.151	0.173
H	0.015	0.025	0.038	0.047	0.065	0.084	0.103	0.118	0.126	0.143	0.155	0.175
I	0.013	0.027	0.039	0.048	0.062	0.076	0.094	0.108	0.117	0.132	0.144	0.165
J	0.016	0.033	0.052	0.055	0.058							
K	0.01	0.026	0.036	0.048	0.064	0.081	0.098	0.112	0.121	0.134	0.147	0.163
L	0.008	0.018	0.03	0.044	0.06	0.077	0.095	0.107	0.118	0.131	0.144	0.158
M	0.015	0.022	0.038	0.05	0.068	0.087	0.095	0.111	0.124	0.14	0.154	0.172
O	0.004	0.016	0.034	0.056	0.073	0.081	0.088	0.101	0.112	0.125	0.137	0.143
P	0.011	0.025	0.038	0.049	0.061	0.079	0.099	0.114	0.125	0.139	0.152	0.165
R	0.012	0.023	0.035	0.048	0.065	0.081	0.099	0.113	0.125	0.141		

Fig. 1 shows the losses of the various alloys which were exposed in the smoke jack for a period of 4 years. The alloys with a complex structure show high losses and the same is apparently true of the high copper-tin alloys. The graph also indicates that as the zinc content of

the alloy is increased to at least 20 per cent., the corrosion resistance of the alloy is helped.

The addition of lead to the alloy appears not to have any pronounced effect on its resistance to corrosion. The addition of tin to a high copper-zinc alloy (low brass) increases its resistance to corrosion and also aids its physical properties. This beneficial effect is limited to the point where a second constituent is formed as, for instance, in alloy C.

It will be appreciated that the accuracy of the present data is not sufficient to permit definite conclusions as to the exact relative position of alloys such as N and P.

Alloys of copper and nickel are less resistant to the action of smoke than any of the ordinary red brasses, although an addition of some nickel to a low brass appears to have a beneficial influence (note alloy L).

TABLE 4.—*Losses of Surface of Catenary Clips Exposed in Service*

	N. Y., N. H. & H. Ry., Test No. 1			B. & M. Ry., Test No 2		
	Ounces per Square Inch					
Alloy No.	7 Mo.	33 Mo.	50 Mo.	7 Mo.	33 Mo.	50 Mo.
A	0.0003	Failed				
C	0.0002	0.005	0.006	Gained	0.003	0.002
F	Samples lost			0.0004	0.0035	0.0045
G	Gained	0.005	0.004			
H	0.004	0.0045	0.004	Gained	0.0035	0.0055
I	Gained	0.005	0.006	Gained	0.0035	0.0055
K	0.0001	0.005	0.007	Gained	0.0025	0.003
L	0.0005	0.0045	0.0065	0.001	0.0055	0.0045
M	0.0003	0.005	0.007	Gained	0.004	0.005
P				0.00045	0.006	0.0045
Q	0.0045	0.009	0.013	Gained	0.006	0.004
S	0.0001	0.004		0.0001	0.007	0.005

Table 4 shows the losses in ounces per square inch of the original surface of the catenary clips which had been in service for a period of about 4 years on the New York, New Haven and Hartford R. R., and the Boston and Maine R. R. These losses are also shown in Fig. 2. The losses due to corrosion during this period under the severest kind of service were almost negligible.

Fig. 3 shows cast catenary clips which were given the accelerated smoke jack test for 24 months. Data regarding the photographs are given in Table 3. Several stamped catenary clips and two pieces of stainless steel messenger wire samples in contact with copper, which

were given the accelerated test for a period of 24 months, are shown in Fig. 4.

The data on the stainless steel, wrought iron and pure iron samples are not given. Due to some discrepancies in the original data, weight of the samples when new could not be definitely established. However, Fig. 4 indicates definitely that the corrosive action is most severe on both the wrought iron and the pure iron samples.

The stainless steel clip resisted the corrosive action of smoke quite well. The stainless steel messenger wire likewise resisted the corrosive action of the smoke except at the point where it was in contact with copper wire. At this point, severe electrolytic corrosion took place.

After corrosion some of the alloys showed a very smooth surface and this is especially true of the rolled materials.

Chemical analyses were made of the soot and the products of corrosion that adhered to the specimens removed from the smoke jack and some of the results are given in Table 5.

TABLE 5.—*Composition of Soot Collected on Specimens in Smoke Box*

	After 1st Month				After 2nd Month				After 7th Month			
Code No.	Cu, Per Cent.	Sn and Ash, Per Cent.	Pb, Per Cent.	Zn and C, Per Cent.	Cu, Per Cent.	Sn and Ash, Per Cent.	Pb, Per Cent.	Zn and C, Per Cent.	Cu, Per Cent.	Sn and Ash, Per Cent.	Pb, Per Cent.	Zn and C, Per Cent.
A	17.5	7.0	Nil	76.0	9.5	7.7	Nil	83.00	19.50	7.60	Nil	73.0
C	24.6	5.6	5.2	65.0	28.5	6.6	5.8	59.00	35.80	9.00	4.3	51.0
D					13.0	0.03	Nil	86.00	19.00	4.30	Nil	64.0
F	28.0	4.0	Nil	67.0	28.0	5.7	Nil	65.76	42.83	6.03	Nil	51.0
G	27.0	7.0	1	64.0	32.0	5.5	1.0	61.50	38.80	9.50	1.5	50.2
H	34.2	7.3	1.3	57.2	33.6	5.1	Nil	61.30	38.80	7.70	1.5	51.0
K	33.5	5.9	1.9	58.7	39.0	5.5	1.7	53.80	40.40	8.00	2.0	49.6
L	25.5	5.0	(Ni, 12.5)	57.5	22.8							
M	18.8	7.5	4.1	69.5	38.0	4.2	6.3	51.50	37.10	7.20	4.9	50.8
P					24.6	5.2	Nil	70.20	42.40	5.00	Nil	52.6

DISCUSSION OF RESULTS

It is felt that this test gives quite definite indications of the relative expected life of the various nonferrous alloys available for overhead construction for railroads operating both steam and electric locomotives. However, it appears that the data obtained are not sufficiently conclusive as to the exact positions of the various similar alloys with regard to each other.

Eliminating those alloys in which a disintegration in structure takes place, the loss of weight data alone does not answer the question as to

the choice of a particular alloy. Such an alloy may successfully resist corrosion but lack the necessary physical strength. For this reason, a compromise must be made which will provide the necessary corrosion resistance and the physical properties required in the particular application.

For example, the alloy of 80 per cent. copper, 2 per cent. tin, 18 per cent. zinc has been found to resist to a remarkable degree corrosive action of smoke. In the cast state its tensile strength is fairly high, yet the yield point is too low. Consequently, this alloy would be less suitable for catenary clips which are cast than are a number of other alloys.
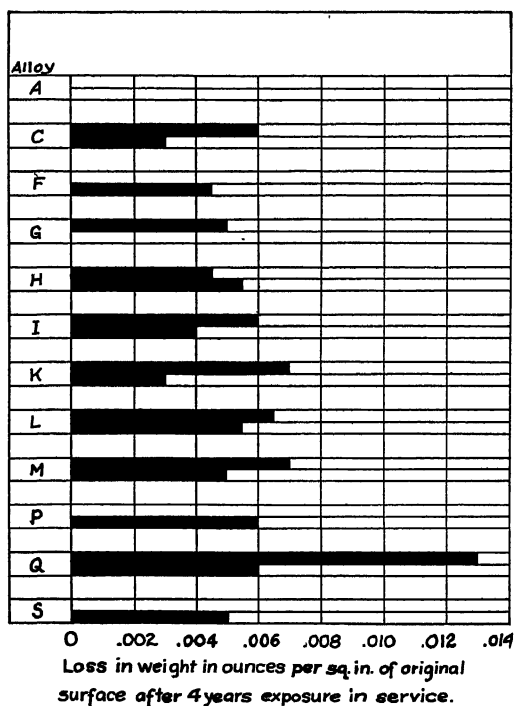
FIG. 2.—LOSS IN WEIGHT OF ORIGINAL SURFACE DURING SERVICE.

An alloy composed of 88 per cent. copper, 8 per cent. tin, 4 per cent. zinc, besides making an excellent casting for this purpose, affords sufficient protection from corrosion, but the price is high. However, if the fitting can be designed for a stamping instead of a casting, then the 80 per cent. copper, 2 per cent. tin, 18 per cent. zinc alloy is worthy of consideration. The combination of its lower price, physical and corrosion-resisting qualities make it practical for actual use.

Other circumstances are encountered with messenger and trolley wire splicers. Some types can be made only in the form of castings, even though weight is a constantly limiting factor. In this case, emphasis

must be placed on the physical properties combined with a high degree of resistance to corrosion.   Price is of secondary importance.

There is too great a tendency to believe that chemical specifications alone are sufficient to guarantee the satisfactory performance of a given

FIG. 3.—CAST CATENARY CLIPS AFTER 24 MONTHS OF EXPOSURE IN SMOKE JACK.

fitting.   Obviously, this is untrue when the extreme sensitiveness of some alloys to foundry practice is considered.   Unless these factors are well appreciated and understood, castings with erratic physical properties are certain to be received.

For example, an alloy of the composition 84 per cent. copper, 3 per cent. tin, 3 per cent. lead, 10 per cent. zinc has very good physical properties and resists smoke corrosion very well. However, the temperature at which this metal is poured into castings has a decided influence upon
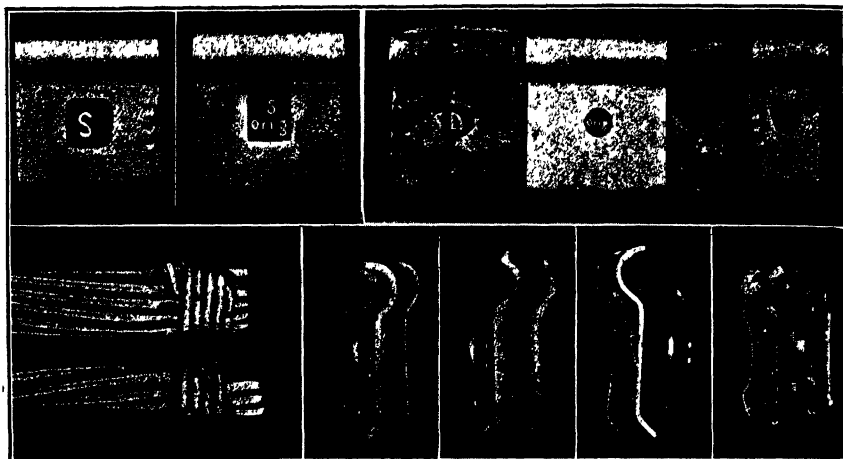
FIG. 4.—CATENARY CLIPS AND MESSENGER WIRE.

Upper row: Stamped catenary clips before and after exposure, alloys S, D and pure iron.
    Lower left: Stainless messenger wire in contact with copper.
    Lower right: Stamped catenary clips: wrought iron, stainless steel, alloy D and J.

its physical characteristics (Table 6). The test was made by pouring a series of standard A. S. T. M. test bars from the same ladle of metal at varying temperatures.

TABLE 6.—*Effect of Pouring Temperature on Physical Properties of Alloy I, 84-3-3-10*

Pouring Temperature, Deg. F.	Ultimate Tensile Strength, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Elongation, Per Cent.	Reduction of Area, Per Cent.	Brinell Hardness, 500 Kg.
2,300	16,850	8,000	11.7	15.2	32
2,100	28,450		23.5	15.3	55.5
2,050	31,650	12,500	26.1	32.8	56
2,000	31,175		29.0	22.8	53

RELATIONSHIP OF SERVICE TEST AND ACCELERATED TEST

It is not yet possible to express in definite figures the relationship between service tests and accelerated tests. The ratio is entirely dependent upon the severity of the corrosive conditions. The samples in service on the New York, New Haven and Hartford R. R. (Fig. 2), with one

unaccounted for exception, show a slightly higher loss than the same service samples on the Boston and Maine R. R. However, the 4-year-period losses in both cases are so small that the differences encountered are chargeable to the natural errors of experimental measurement of this nature.

In making a comparison between the loss in weight figures of the various alloys in the accelerated test and those in actual service, it is estimated roughly that 1 month of exposure in the smoke jack corresponds to about 2 years of moderately severe service.

The time a given alloy should last on electrified steam road service cannot be determined by consideration of the corrosion-resisting properties alone. It is a question of which alloy will best resist the corrosive smoke action, provide the required physical properties, and can be purchased at a reasonable price.

In these tests certain stainless steels with remarkable corrosion-resisting qualities have been found. Yet, so difficult are the commercial manufacturing problems which they present that their prices compare unfavorably with nonferrous alloys with equal corrosion-resisting properties. There is also introduced another difficulty which easily might be overlooked. Electrolytic corrosion takes place when ferrous and nonferrous metals are in contact in the presence of an electrolyte, a condition which is plainly indicated by the stainless steel messenger in contact with a copper fitting in Fig. 4.

Catenary materials for steam road electrification should have the same or nearly the same electrolytic potential. This limits the selection to copper and proper copper alloys.

The information obtained from this test is not only very interesting but already has been utilized commercially with success. It is recognized that many desirable factors have not been considered and evaluated; a work which remains to be done. From this viewpoint, these data are open to criticism. However, they provided the reason for another accelerated test which has been progressing for about a year. The specimens under test are in the form of standard A. S. T. M. test bars, both round and flat. These specimens will not only enable us to check accurately the corrosion losses but also to determine how and what physical properties of the samples are being affected.

A list of the specimens is given in Table 7, and most of the specimens that are being tested are shown in Fig. 5. Another series of service tests at Cleveland, Ohio, is planned to begin with the completion of the Cleveland Terminal electrification project.

Fig. 6 shows one of the series of test pieces which were removed from the smoke jack at intervals of 2 months. This arrangement permits the removal of test specimens for the periodic check without disturbing the remainder. About 4 years will be required to complete the test now in progress.

TABLE 7.—*Specimens under Accelerated Test Now in Progress*

ALLOY	SPECIMEN
OB Alloy No. 1	Flat
OB Alloy No. 1	Round
OB Alloy No. 1A	Flat
OB Alloy No. 1A	Round
OB Alloy No. 4B	Flat
OB Alloy No. 4B	Round
OB Alloy No. 5	Flat
OB Alloy No. 5	Round
OB Alloy No. 5A	Flat
OB Alloy No. 5A	Round
OB Alloy No. 5B	Flat
OB Alloy No. 5B	Round
OB Alloy No. 6	Flat
OB Alloy No. 6	Round
OB Alloy No. 16	Flat
OB Alloy No. 16	Round
OB Alloy No. 17	Flat
OB Alloy No. 17	Round
OB Alloy No. 20	Flat
OB Alloy No. 20	Round
OB Alloy No. 1200	Flat
OB Alloy No. 1200	Round
Cast Everdur	Flat
Cast Everdur	Round
Cast Aluminum No. 12	Flat
Cast Aluminum No. 12	Round
Cast Aluminum No. 47	Flat
Cast Aluminum No. 47	Round
OB pure aluminum	Flat
OB No. 1 machined	Round
OB No. 5 machined	Round
OB No. 20 machined	Round
Al bronze, Lumen Bearing Co	Round
OB mall. iron, flecto and galvanized	Flat
OB mall. iron, flecto and galvanized	Round
OB mall. iron and copper 1.03	Flat
OB mall. iron and copper 1.03	Round
OB mall. plain flecto	Flat
OB mall. plain flecto	Round
Monel cold-rolled	Flat
Monel hot-rolled	Flat
Everdur rolled	Flat
Hardware bronze	Flat
Phono elec. rolled, PDS 148	Flat
Copper cold-rolled	Flat
Red Brass, Anaconda, mix No. 35	Flat
OB 1A, poured 2300	Flat
OB 5, poured 2300	Flat
Copper weld	Flat
Copper weld	Round

TABLE 7.—(Continued)

ALLOY	SPECIMEN
Basic open hearth	Flat
Basic open hearth	Round
Aluminum bronze rolled	Flat
Aluminum bronze rolled	Round
Ascaloy	Flat
Ascaloy	Round
Super Ascaloy	Flat
Armco	Round
Stainless iron	Round
Wrought iron	Round
Wrought iron	Flat
Super Ascaloy	Round
Stainless steel	Flat
Stainless steel	Round
Resistal	Flat

The values for ultimate tensile strength as well as yield point have been calculated by dividing the actual yielding and breaking load by
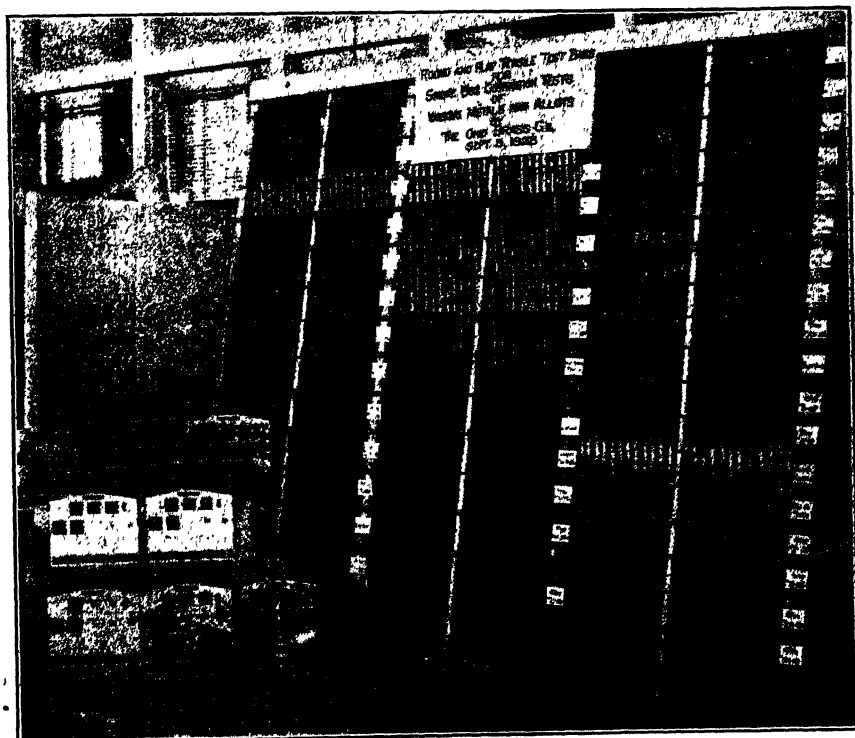
FIG. 5.—SPECIMENS UNDERGOING ACCELERATED TEST.

the cross-section of the test specimen which was determined on the specimen before it was subjected to the corrosion test. This was done

because the strength of a metallic appliance is reduced in amounts proportional to the material lost by corrosion. Physical properties thus expressed enable the designer to calculate sections needed to withstand a given stress, allowing at the same time for the loss of material due to corrosion over a definite time.

FIG. 6.—TEST PIECES REMOVED FROM SMOKE JACK AT 2-MONTH INTERVALS.

The specimens are identified by a code system consisting of various numbers of drill marks. It has been found that the drill marks can be identified easily almost up to the moment when the specimens are broken away.

CONCLUSION

As previously stated, the results given are not entirely conclusive. They give an indication of the relative value of various types of alloys commercially available for overhead construction work for steam road electrification purposes.

The conclusion that some alloys which stand up well under various other forms of corrosion have failed to stand up when subjected to the corrosive action of locomotive smoke also appears justifiable.

ACKNOWLEDGMENTS

Internal Stress and Season Cracking in Brass Tubes

By D. K. Crampton,* Waterbury, Conn.

INTERNAL stress and season cracking in brass have been studied for many years and the technical literature contains many data on various phases of the subject. A résumé of the literature shows certain fairly well established points upon which various authors are mostly agreed:

1. Season cracking is primarily caused by the presence of relatively high internal stresses, or possibly in some cases by external stresses, or both.

2. A specific corrosion is also essential to season cracking. Certain agents, particularly mercurous salts, mercuric salts and ammonia salts, have such a specific corrosive effect.

3. The tendency to season crack under given conditions increases with increasing zinc content, brass containing less than 20 per cent. zinc being relatively immune.

4. In alpha brass the season cracks are intercrystalline; in alpha-beta brass they lie between the two constituents; and in beta brass they are transcrystalline.

5. The ordinary impurities or added elements in special brasses have little or no effect on the tendency to season crack.

6. Internal stresses can be eliminated, or at least reduced to a safe limit by annealing treatments at temperatures that do not produce visible microstructural changes or appreciable softening of the worked brasses.

There are, however, some points in connection with the phenomenon of season cracking which have not been thoroughly investigated, or wherein different authors and investigators are not entirely in agreement. The investigations described in this paper were undertaken to determine:

1. The correlation between mercurous nitrate tests and actual season cracking on long-time atmospheric exposure.

2. The quantitative effect of type and degree of drawing operations on the intensity of internal stress and on the tendency to season crack in brass tubes.

3. The possibility of drawing high-brass tubes in such a manner as to prevent the occurrence of harmful stresses rather than to find a remedy for such stresses once having obtained them.

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PRELIMINARY TESTS FOR MEASUREMENT OF STRESS

As it was desirable to have a simple method for comparing the relative intensity of internal stress in different tubes, a careful review was made of the methods described in the literature.   The method of Heyn and Bauer[1] and especially the more general method of Sachs[2] are, of course, the proper ones if a complete understanding of the intensity and distribution of stress is desired.   The objection to using these methods for comparison of numerous samples is that they require a prohibitively long and tedious procedure.   Therefore it seemed that the general method proposed by Hatfield and Thirkell[3] would best serve the purpose.   This
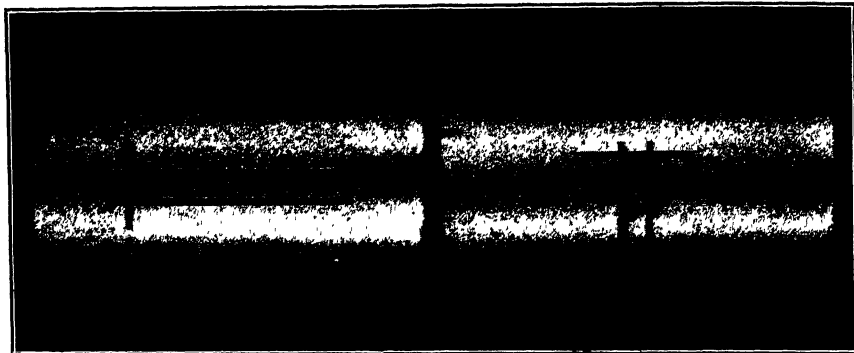
FIG. 1.—TYPE OF SPECIMEN USED FOR ESTIMATION OF INTERNAL STRESS IN BRASS TUBES BY ANDERSON AND FAHLMAN'S METHOD.

FIG. 2.—TYPE OF SPECIMEN USED FOR ESTIMATION OF INTERNAL STRESS IN BRASS TUBES BY HATFIELD AND THIRKELL'S METHOD.

method consists essentially in cutting rings, splitting them along one element and then measuring the change in radius of curvature.   This method was examined by Anderson and Fahlman[4] and condemned for drawn brass tubes.   They say: "In the case of lots of tubing examined, machining tests made by Heyn's method and by that of Hatfield and Thirkell failed to disclose any evidence of stress."   Also: "The machining test suggested by Hatfield and Thirkell was found to be not applicable to the tubing, but a modified form of it was devised.   Thus a piece of tubing was split halfway round its circumference in three places so as to test the entire circumference for stress.   One end of each of the split strips was set free by cutting.   No springing out, or moving in

[1] Heyn and Bauer: Über Spannungen in kaltgerechten Metallen. *Int. Ztsch. Metallog.* (1911) **1**, 16.

[2] Von G. Sachs: Der Nachweis innerer Spannungen in Stangen und Rohren. *Ztsch. f. Metallkunde* (1927) **19**, 352.

[3] Hatfield and Thirkell: Season Cracking. *Jnl.* Inst. Metals (1919) **22**, 67.

[4] Anderson and Fahlman: A Method for Measuring Internal Stress in Brass Tubes. *Jnl.* Inst. Metals (1924) **32**, 367.

any direction, occurred. This indicates absence of circumferential stress." They further draw the conclusion that usually circumferential stresses are absent, or at any rate that the major stress is longitudinal. Sachs, however, found that the tangential stresses were materially higher in certain tubes than were the longitudinal stresses. Certainly it seems logical to assume that, since longitudinal cracks prevail in drawn tubes, these are caused by tangential stresses which must be greater than the longitudinal stresses.

In some preliminary tests with various modifications of the splitting-ring method of Hatfield and Thirkell, and the strip method of Anderson and Fahlman, it was discovered that the width of the strips, whether longitudinal or circumferential, had a profound effect on the degree of springing out and therefore on the calculated stress. In a high-brass tube which had been drawn from 2½ in. O.D. by ⁵⁄₃₂ in. wall thickness to 2⅛ in. O.D. by ⅛ in. wall thickness, longitudinal and circumferential strips were milled as described by Anderson and Fahlman. The width of the circumferential strips so milled varied from ¹⁄₁₆ to 2 in., while the width of the longitudinal strips varied from ¹⁄₁₆ to ½ in. Fig. 1 shows a typical longitudinal strip and Fig. 2 a typical circumferential strip. The apparent internal

FIG. 3.—EFFECT OF WIDTH OF STRIP ON APPARENT INTERNAL STRESS CALCULATED BY HATFIELD AND THIRKELL'S AND ANDERSON AND FAHLMAN'S METHODS.

stress in the circumferential strips was calculated according to the formula given by Hatfield and Thirkell

$$S = \frac{Et}{2}\left(\frac{r_1 - r_2}{r_1 \, r_2}\right)$$

and the stress in the longitudinal strips calculated by the formula given by Anderson and Fahlman

$$S = \frac{Eti}{l^2}$$

where S = internal stress, lb. per sq. in.
  E = modulus of elasticity (here assumed to be 15,000,000 lb. per sq. in.)
  t = wall thickness, inches
  r_1 = final mean radius of curvature, inches
  r_2 = initial mean radius of curvature, inches
  i = amount of spring out of strip, inches
  l = length of strip, inches

The results of these preliminary tests are given in Table 1 and shown graphically in Fig. 3.

TABLE 1.—*Stress Measurements*

CIRCUMFERENTIALLY MILLED STRIPS

Width of Strip, Inches	Original Outside Diameter, Inches	Final Outside Diameter, Inches	Calculated Internal Stress, Lb. per Sq. In.
1/16	2.1265	2.1300	1590
1/8	2.1265	2.1330	3100
1/4	2.1265	2.1355	4130
1/2	2.1265	2.1375	5180
1	2.1265	2.1425	7520
2	2.1260	2.1510	11700

LONGITUDINALLY MILLED STRIPS

Width of Strip, Inches	Original Outside Diameter, Inches	Springing Out of Strip, Inches	Length of Strip, Inches	Calculated Internal Stress Lb. per Sq. In.
1/16	2.1330	0.056	2¾	13,900
1/8	2.1330	0.073	2¾	18,100
1/4	2.1310	0.081	2⅝	22,000
1/2	2.1310	0.067	2½	19,600

It will be seen from Table 1 and Fig. 3 that the apparent circumferential stress increases continuously with increasing width of the circumferential strips cut. In the longitudinal strips, the apparent stress increases up to strips 1/4 in. wide and then falls off. This falling off is apparently due to the diminution of the springing out of the strips which is caused by the stiffening effect of the transverse curvature. It is probable that, lacking this transverse curvature effect, there would be a continuous increase as with the circumferential strips.

TABLE 2.—*Calculated Stress Obtained by Splitting Sections of Tubes of Varying Lengths*

Length of Test Section, Inches	Calculated Internal Stress, Lb. per Sq. In.	Length of Test Section, Inches	Calculated Internal Stress, Lb. per Sq. In.
0.080	6,790	0.815	9,620
0.095	6,480	1.125	11,200
0.110	7,100	1.75	13,000
0.280	7,400	3.50	13,700
0.310	7,730	5.50	16,100
0.400	7,730	18.0	15,100
0.610	8,360		

Undoubtedly the failure of Anderson and Fahlman to get the results they expected by Hatfield and Thirkell's method should be attributed to their having used strips that were too narrow. In fact, this same criticism must be made of their own strip method for longitudinal stress or any method involving the use of such narrow strips.

Inasmuch as circumferential stresses were apparently more important in drawn tubes than longitudinal stresses, it was decided to use a circumferential stress measurement for comparison of various lots of tubing and a further simplification of Hatfield and Thirkell's method, using wider strips, was sought. Instead of milling strips circumferentially, a tube of a given length was split along one element for its
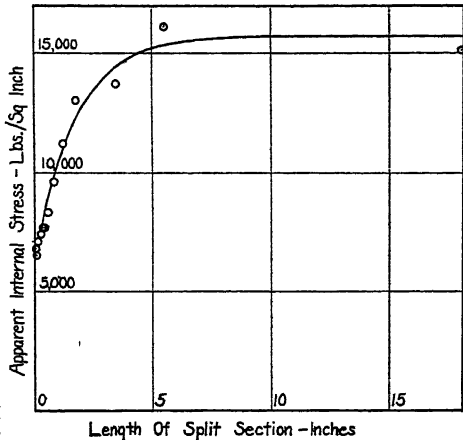
FIG. 4.—EFFECT OF LENGTH OF SPLIT SECTION ON APPARENT INTERNAL STRESS IN A BRASS TUBE OF 2 IN. DIAMETER.
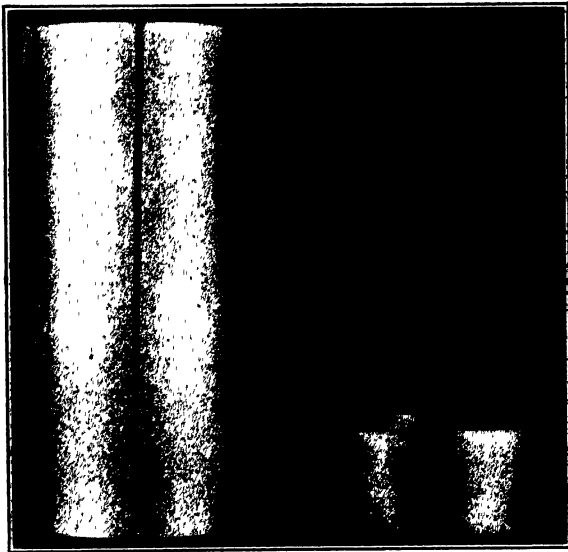
FIG. 5.—TYPE OF SPECIMEN USED FOR ESTIMATION OF INTERNAL STRESS BY MODIFICATION OF HATFIELD AND THIRKELL'S METHOD.

entire length by a simple saw cut. Another portion of the same tube used in the experiment described in Table 1 and Fig. 3 was investigated

by this method, using lengths varying from about the shortest thàt could be cut conveniently up to some 18 in. long.   All of these were split by sawing along one element and the stress was calculated as with the milled circumferential strips.   The results of this experiment are given in Table 2 and shown diagrammatically in Fig. 4.   The type of tube sample used is illustrated in Fig. 5.

Several other tubes of various initial sizes and degrees of working were investigated in the same way with much the same results.   In all cases the apparent circumferential strèss increased with increasing lengths of tube section up to a length somewhere about 2½ to 3 times the diameter of the tube.   With greater lengths, little or no increase in apparent stress was evident.   The use of a split section of this type where the length tested was at least three times the diameter was therefore adopted as a means of comparing stresses ìh differently treated tubes.   A standard length of 3 in. was used in the following investigation, all tubes tested having outside diameters of 0.719 to 0.953 in.   The ratio of length to diameter was therefore 4.2 to 3.15.

EFFECT OF VARIATION IN ANALYSIS ON INTERNAL STRESS AND SEASON CRACKING

In this series of tests, tubes were prepared with copper content varying from 59.67 to 94.02 per cent.; lead from 0.01 to 1.26 per cent.; iron from 0.02 to 0.15 per cènt.; and tin from 0 to 0.94 per cent.   All of these tubes were carefully drawn on the same mill schedule to 1 in. O. D. by 0.060 in. wall thickness.   The tubes were next carefully annealed at approximately 600° C. and were then sunk, using, a $1\frac{3}{16}$ in. dia. die having a 20° entrance angle and ⅛ in. bearing.   No plug was used.   On the tubes so treated the following tests were made:

1. Rockwell hardness tests on the inside surface of split portions.

2. Circumferential stress measurements in duplicate by the method described above.

3. Mercuŗǫùs nitrate tests in triplicate on 3-in. lengths, observing the time reqùired for the initial appearance of cracks.   The standard mercurous nitrate solution containing 100 g. of mercurous nitrate and 13 c.c. of concentrated nitric acid per liter of water was used.   New solution was used for each test.

4. Two 8-in. lengths of each tube were suspended on the roof of the laboratory for periodic examination for appearance of season cracks.

5. Two 10-ft. lengths of each type of tube were annealed on a Snead electric resistance annealer, giving an extremely rapid heating effect. The object of this test was to check the susceptibility to so-called "fire cracking."

The results of all tests on this series of alloys are brought together in Table 3. In this table the average values only of each particular measurement are given with the exception of the time required for roof-exposure samples to show normal season cracking, which values are given separately.

TABLE 3.—*Properties of Brass Tubes of Varying Analyses*
Hollow Sunk From 1 in. O.D. by 0.060 in gage to 0.813 in. O.D.

| Tube No. | Analysis, Per Cent. | | | | Mean Rockwell Hardness (16-60-B) | Mean Internal Circumferential Stress, Lb. per Sq. In. | Mean Time to Crack in Standard HgNO₃ Sol. Minutes | Reciprocal of Time to Crack in HgNO₃ | Time to Crack on Atmospheric Exposure, Days | | Behavior on Snead Electric Annealer |
	Cu	Pb	Fe	Sn					Sample A	Sample B	
1	59.67	0.04	0.06		103	52,900	0.24	4.17	56	63	OK
2	63.55	0.04	0.03		99.5	46,000	0.41	2.44	*a*	*a*	OK
3	66.50	0.03	0.03		99	47,400	0.42	2.38	339	577	OK
4	70.37	0.04	0.03		101	44,700	0.45	2.22	324	339	OK
5	78.22	0.02	0.04		99.5	47,500	4.67*c*	0.21	*a*	*a*	OK
6	89.26	0.02	0.02		95.5	39,100	1210*c*	0.0008	*a*	*a*	OK
7	94.02	0.01	0.03		92	36,800	*b*	0	*a*	*a*	OK
8	65.90	0.28	0.02		102	44,500	0.58	1.72	324	*a*	Cracks entire length
9	66.00	0.56	0.04		100.5	48,000	0.42	2.38	339	*a*	Cracks entire length
10	65.82	0.74	0.05		100	48,000	0.43	2.33	*a*	*a*	Very bad cracks entire length
11	65.90	0.95	0.05		101	47,800	0.30	3.33	238	294	Extremely bad cracks entire length
12	65.50	1.26	0.06		100	51,800	0.42	2.38	210	*a*	Extremely bad cracks entire length
13	65.57	0.05	0.04		99	47,400	0.38	2.63	238	339	OK
14	66.23	0.04	0.09		98.5	46,200	0.56	1.79	294	*a*	One slight crack
15	65.58	0.04	0.13		100.5	50,800	0.38	2.63	294	*a*	OK
16	66.30	0.04	0.15		101	52,000	0.57	1.75	210	238	One slight crack
17	66.22	0.03	0.03	0.24	98	44,600	0.64	1.56	*a*	*a*	OK
18	65.92	0.04	0.03	0.50	100	44,500	0.96	1.06	*a*	*a*	OK
19	65.02	0.02	0.06	0.68	98	42,600	0.71	1.41	*a*	*a*	OK
20	65.68	0.04	0.03	0.94	99	42,900	0.66	1.52	*a*	*a*	OK

a Has not cracked in 40 months. *c* All three specimens split from end to end with explosive violence.
b Did not crack in 100 hours.

In Fig. 6 are plotted the internal circumferential stresses obtained in the tubes of varying copper content, the reciprocal of the time required for these tubes to crack in standard mercurous nitrate solution, and the Rockwell hardness. In this test the 1/16 in. ball, 60-kg. load and B scale were used (16-60-B). In Fig. 7 are plotted the reciprocals of the times required to crack in standard mercurous nitrate solution for the tubes in

the lead, iron and tin series.   In all these tests it was assumed that the tendency to season crack would vary approximately inversely as the time at which the first crack became visible in a mercury test.   In using and plotting the tests, therefore, the reciprocal of the time in minutes was used rather than the actual time itself.

A study of Table 3 and Figs. 6 and 7 shows some very interesting phenomena:

1. The Rockwell hardness and the apparent circumferential stress, as determined by the method used, increase appreciably as the copper content of brass tubes is reduced from approximately 95 per cent. down to approximately 60 per cent.   It appears that the variation in stress is closely connected with the variation in intrinsic hardness of these various alloys.   In other words, for identically the same drawing and preliminary annealing treatment it
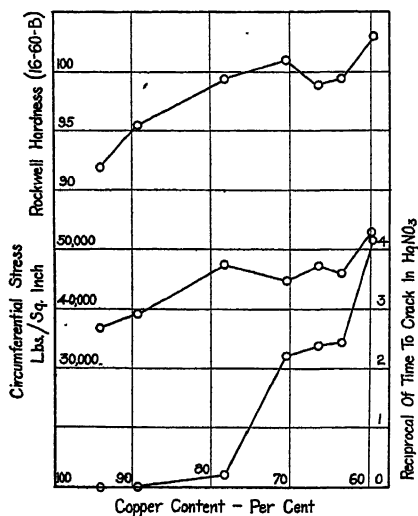
FIG. 6.—EFFECT OF COPPER CONTENT ON INTERNAL STRESS AND TENDENCY TO SEASON CRACK IN BRASS TUBES SUNK FROM 1 IN. BY 0.060 IN. TO 0.813 IN.
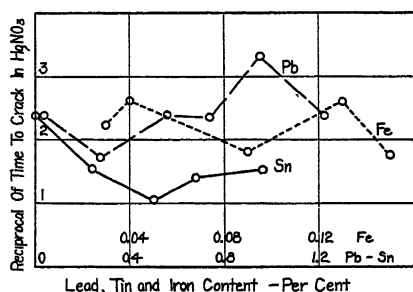
FIG. 7.—EFFECT OF LEAD, TIN, AND IRON CONTENT ON INTERNAL STRESS AND TENDENCY TO SEASON CRACK IN BRASS TUBES SUNK FROM 1 IN. BY 0.060 IN. TO 0.813 IN.

seems that rather higher internal stresses result in tubes of naturally greater hardness.

2. A marked variation in time required to crack in mercurous nitrate solution is found with tubes of varying copper content.   Under the conditions described it was impossible to crack tubes of 94.02 per cent. copper content.   Those of 89.26 per cent. copper cracked only after a very long exposure.   It is, however, interesting to note that when such tubes finally cracked they did so with explosive violence.   This is sharply in contrast with the action of the high-zinc alloys, which invariably cracked and opened quietly.   Tubes of 78.22 per cent. copper content cracked after an intermediate exposure and these also cracked with considerable force.   From this point to 59.67 per cent. copper there is a marked increase in the tendency to crack.

3. The tests on the lead and iron series do not show very clean-cut tendencies. The tin series, however, shows an appreciable diminution of tendency to crack with increasing tin content.

4. It was not expected that a very precise quantitative agreement would be obtained between the results of mercurous nitrate tests and atmospheric exposure tests. There was found, however, a gratifying qualitative agreement between these two tests. The tubes that showed the lowest tendency to season crack as measured by the mercurous nitrate test have not cracked to date after an exposure of 3 years and 4 months. In those that have cracked on the exposure test the order of cracking has been, in general, in agreement with that found in the mercurous nitrate test. Note that both samples of tube No. 1, having distinctly the highest value for $\frac{1}{T}$ in the mercurous nitrate test, season cracked on exposure in a much shorter time than any of the others. Also, the exposure tests indicate no difference in season cracking tendency with variations in lead or iron content. Perhaps one of the most significant features is that none of the tin-bearing tubes (Nos. 17 to 20 incl.) cracked on exposure, indicating that the presence of tin has a marked protective effect. This checks with the fact that these same tubes show a lower value for $\frac{1}{T}$ in the mercurous nitrate test (see Table 3 and Fig. 7) than the tin-free alloy or any of the lead-bearing or iron-bearing series.

These results strongly suggest that mercurous nitrate tests, with careful measurements of time to crack, are reasonably reliable in foretelling the probable season cracking tendencies of internally stressed brass tubes.

5. The results of the tests on the Snead electric annealer are especially interesting. It is obvious that increase in lead content drastically increases the tendency to fire cracking and there is some slight indication that increase in iron content has a similar but lesser effect. There appears to be some fundamental difference between the mechanism of so-called fire cracking and that of season or corrosion cracking, as the mercurous nitrate and exposure tests do not indicate any particular influence of the lead content. It is impossible to draw any specific conclusions as to the relative tendency to fire crack for various copper contents and tin contents, as none of those tubes cracked on annealing.

EFFECT OF TYPE AND DEGREE OF DRAWING REDUCTION ON INTERNAL STRESS AND SEASON CRACKING

In this series of experiments it was necessary to have a considerable quantity of tubing of practically identical analysis. Common high brass with a moderate lead content was used. Material from three

furnace heats was required and the analyses of the three heats used were as follows:

Heat No.	Copper, Per Cent.	Lead, Per Cent.	Iron, Per Cent.	Zinc, Per Cent.
1	66.28	0.29	0.03	Remainder
2	66.30	0.31	0.03	Remainder
3	66.15	0.34	0.03	Remainder
Average	66.24	0.31	0.03	Remainder

Three series of reductions were made from the initial sizes which were: Outside diameter, 1 in.; series A., wall thickness, 0.025 in. 1; series B, wall thickness, 0.060 in.; series C, wall thickness, 0.150 inches.

After drawing to these three initial sizes, all the tubing was carefully annealed in the mill as uniformly as possible at a temperature of approximately 600° C. For the final reductions, either by drawing or sinking, to the sizes on which stress and mercurous nitrate tests were to be made, a series of carefully prepared dies was made up. All had a 20° entrance angle and $\frac{1}{8}$-in. bearing. The diameters of these finishing dies were as follows:

Inch	Inch		Inch	Inch
$6\frac{1}{64}$	0.953		$1\frac{3}{16}$	0.813
$2\frac{9}{32}$	0.906		$4\frac{9}{64}$	0.766
$5\frac{5}{64}$	0.859		$2\frac{3}{32}$	0.719

For each die size and each initial tube size a series of reductions was made from about the lightest to about the heaviest that could be given the tube in question. It will thus be seen that the tubes actually tested cover a wide range of initial size and of type and degree of cold drawing.

The tests and observations made on the tubes in this series comprise the following:

1. Rockwell hardness (5 to 10 checks),
2. Apparent circumferential stress (2 checks),
3. Time to crack in standard mercurous nitrate solution (3 checks),
4. Action on Snead electric annealer (2 checks),
5. Time to crack on atmospheric exposure (2 checks).

The results of this series of tests are brought together in Tables 4, 5 and 6. In these tables in the columns headed "Action on Snead Electric Annealer" it will be noted that a number of tubes were not annealed. With the tubes drawn and sunk from 1 by 0.025 in., excessive difficulty was encountered due to burning through at the contact on these very thin walls. With the tubes drawn and sunk from 1 by 0.15 in., difficulties of another kind were met. Here the tubes in question did not have sufficient resistance to heat rapidly and the capacity of the machine was overtaxed.

A study of Tables 4, 5 and 6 will show that the Rockwell hardness bears no apparent relation to the circumferential stress, or to the tendency to season crack as measured by the mercurous nitrate test, exposure tests,

TABLE 4.—*Properties of High-brass Tubes Drawn and Sunk from 1.001 in. O.D. by 0.026 in. Gage*

Tube No.	Final O.D., Inches	Final Gage, Inches	Diameter Reduction, Per Cent.	Area Reduction, Per Cent.	Rockwell Hardness (16-60-B)	Mean Internal Circumferential Stress Lb per Sq. In.	Time to Crack in Standard HgNO₃ Sol. Minutes	Reciprocal of Time to Crack in HgNO₃	Time to Crack on Atmospheric Exposure, Days		Action on Snead Electric Annealer
									Sample A	Sample B	
A1ᵃ	0 952	0 0275	5	3	71.5	15,900	ᵇ	0	ᶜ	ᶜ	OK
A2ᵃ	0.908	0 0275	9	5	76	19,000	21 0ᵈ	0.048	ᶜ	ᶜ	OK
A3	0.906	0.022	9	23	93.5	13,200	53.0	0 019	ᶜ	ᶜ	OK
A4	0 906	0.020	9	30	96	8,100	ᵇ	0	ᶜ	ᶜ	OK
A5	0.905	0.0175	9	38	98 5	3,800		0	ᶜ	ᶜ	OK
A6ᵃ	0 8615	0.028	14	8	79	24,700	0.61	1.64	ᶜ	ᶜ	Not annealed
A7	0.860	0 024	14	20	94	7,300	ᵇ	0	ᶜ	ᶜ	OK
A8	0.8595	0 022	14	27	98	7,900	ᵇ	0	ᶜ	ᶜ	OK
A9	0 859	0 019	14	37	100	6,400	ᵇ	0	ᶜ	ᶜ	OK
A10	0.858	0.016	14	47	101	2,500	ᵇ	0	ᶜ	ᶜ	OK
A11ᵃ	0.8145	0 029	19	9	89.5	33,600	0.32	3.12	ᶜ	ᶜ	One discontinuous crack
A12	0.8125	0.022	19	31	99	4,400	ᵇ	0	ᶜ	ᶜ	Not annealed
A13	0.812	0.020	19	37	100	900	ᵇ	0	ᶜ	ᶜ	Not annealed
A14ᵃ	0.768	0 0295	23	15	93	36,300	0.24	4.17	ᶜ	ᶜ	Not annealed
A15	0.7655	0 0235	23	31	98.5	6,100	ᵇ	0	ᶜ	ᶜ	Not annealed
A16ᵃ	0.7195	0 030	28	19	96	49,100	0.19	5.26	177	199	Not annealed

ᵃ These tubes hollow sunk.
ᵇ Did not crack in 150 hours
ᶜ Has not cracked in 29 months.
ᵈ Cracked circumferentially.

or the action on the electric annealer. In other words, the hardness, and presumably the tensile strength and other physical properties, can not be used as criteria of the intensity of internal stress or tendency to season crack. It is also apparent that the internal stress and the tendency to season crack decrease rather than increase with increasing percentage of reduction of area by drawing.

The tests made on the electric annealer were somewhat disappointing in this series, as all the tubes could not be annealed because of the reasons stated. However, in the ones annealed the greatest tendency to fire crack occurred in those which had been subjected to a heavy sinking operation.

As with the tubes of varying analysis, those of the present series show a good general agreement between the stress determinations, the mercurous nitrate tests, the exposure tests, and the electric annealing

TABLE 5.—*Properties of High-brass Tubes Drawn and Sunk from 1.000 in. O.D. by 0.0615 in. Gage*

Tube No.	Final O.D., Inches	Final Gage, Inches	Diameter Reduction, Per Cent.	Area Reduction, Per Cent.	Rockwell Hardness (16-60-B)	Mean Internal Circumferential Stress Lb. per Sq. In.	Time to Crack in Standard HgNO₃ Sol. Minute	Reciprocal of Time to Crack in HgNO₃	Time to Crack on Atmospheric Exposure, Days		Action on Snead Electric Annealer
									Sample A	Sample B	
B-1[a]	0 9485	0 063	5	3	76 5	17,800	9.83[d]	0 10	c	c	OK
B-2[a]	0.9045	0 064	9	6	87 5	23,500	0 97	1 03	c	c	OK
B-3	0 907	0 0525	9	22	98	16,500	1 05	0 95	c	c	OK
B-4	0 907	0 0475	9	29	100	14,100	2 87	0 35	c	c	OK
B-5	0 906	0.0415	9	38	103	5,900	b	0	c	c	OK
B-6	0 9065	0 036	9	45	104	9,800	b	0	c	c	OK
B-7[a]	0 860	0 065	14	10	93	31,400	0 52	1 92	c	c	OK
B-8	0 860	0 056	14	21	100 5	15,700	1 06	0 94	c	c	OK
B-9	0 8605	0 0505	14	29	101	14,900	1.45	0 69	c	c	OK
B-10	0 860	0 045	14	37	104	12,200	3 87	0 26	c	c	OK
B-11	0 8595	0 0385	14	45	104.5	5,900	b	0	c	c	OK
B-12[a]	0 8125	0 0665	19	14	97 5	37,300	0.32	3.12	c	c	3 or 4 discontinuous cracks
B-13	0.8135	0 0595	19	22	100	14,100	0 43	2 22	c	c	OK
B-14	0 814	0 0535	19	29	103 5	21,100	0 38	2.63	c	c	OK
B-15	0 8135	0 0465	19	38	104	14,100	7 67	0.13	c	c	OK
B-16	0 8125	0.040	19	46	104 5	6,500	b	0	c	c	OK
B-17[a]	0 7665	0 067	23	19	99	48,000	0 23	4.35	238	238	OK
B-18	0 767	0.057	23	30	101 5	18,800	0 32	3 12	c	c	OK
B-19	0 767	0 050	23	38	105	22,500	0 35	2 85	c	c	OK
B-20	0 7655	0 0425	23	47	106	7,900	b	0	c	c	OK
B-21[a]	0 717	0 068	28	24	103	55,000	0.22	4 55	15	51	3 or 4 discontinuous cracks
B-22	0.7185	0 054	28	38	105	25,800	0 40	2 50	465	c	OK
B-23	0 718	0.0455	28	47	107.5	5,900	1680	0 0006	c	c	OK

[a] These tubes hollow sunk.	[c] Has not cracked in 29 months.
[b] Did not crack in 150 hrs.	[d] Cracked circumferentially.

tests.   Of the 59 different tubes of varying size, and varying type and degree of reduction, only one having an internal stress of over 40,000 lb. per sq. in. failed to season crack on exposure in at least one check specimen.   On the other hand, only two having stresses less than 40,000 lb. per sq. in. did season crack, and here in only one of the two check specimens.   Also, with only one exception, all tubes having a value of $1/T$ for the HgNO₃ test greater than 4.20 cracked and with one exception all having less value did not crack.

There is a marked difference in behavior of the tubes drawn from the three different initial sizes.   In general the stresses increase markedly in intensity in going from the thin-walled series (Table 4), to the medium (Table 5), and to the thick-walled series (Table 6).   Comparatively few

TABLE 6.—*Properties of High-brass Tubes Drawn and Sunk from 1.001 in. O.D. by 0.151 in. Gage*

Tube No.	Final O.D., Inches	Final Gage, Inches	Diameter Reduction, Per Cent.	Area Reduction, Per Cent.	Rockwell Hardness (16-60-B)	Mean Internal Circumferential Stress Lb. per Sq In.	Time to Crack in Standard HgNO₃ Sol. Minute	Reciprocal of Time to Crack in HgNO₃	Time to Crack on Atmospheric Exposure, Days		Action on Snead Electric Annealer
									Sample A	Sample B	
C-1a	0.948	0 1525	5	5	89 5	22,600	2.70d	0.37	c	c	Not annealed
C-2a	0.9005	0.1545	10	10	96	32,100	1.10	0.91	c	c	Not annealed
C-3	0.908	0.1305	9	20	99	25,900	0.39	2.56	c	c	Not annealed
C-4	0.9075	0.1165	9	28	102	19,400	0.82	1.22	c	c	OK
C-5a	0.8565	0.1555	14	15	101	36,100	0.35	2.85	c	c	Not annealed
C-6	0.8615	0.142	14	20	101	39,300	0.31	3.23	c	c	Not annealed
C-7	0.8805	0 1235	14	28	104	0	b	0	c	c	Not annealed
C-8	0.861	0.108	14	36	104	20,100	1.74	0.58	c	c	OK
C-9	0 8605	0.0925	14	45	106	14,700	1260	0.0008	c	c	OK
C-10a	0.810	0.1565	19	20	105	49,200	0 22	4.55	238	c	Not annealed
C-11	0 8145	0.1345	19	28	104	28,100	0 21	4 75	660	c	Not annealed
C-12	0.8145	0.116	19	37	105 5	28,900	0.25	4 00	c	c	OK
C-13	0 814	0 097	19	45	108	30,800	0.55	1.82	c	c	OK
C-14a	0.7655	0 1565	23	25	107	52,800	0.19	5 26	15	344	One discontinuous crack
C-15	0.7675	0.1495	23	28	107	46,300	0.22	4 55	134	216	Not annealed
C-16	0.7675	0.1245	23	37	105 5	25,800	0.30	3 33	c	c	Not annealed
C-17	0.7675	0 106	23	45	107	25,100	0 71	1.41		c	OK
C-18a	0.716	0 155	28	32	104	60,100	0 18	5 56	c	c	One discontinuous crack
C-19	0.720	0.1385	28	37	106	65,300	0.19	5 26	153	c	Two discontinuous cracks
C-20	0.7195	0 114	28	45	108	51,800	0 40	2.50		c	OK

a These tubes hollow sunk.
b Did not crack in 150 hours.
c Has not cracked in 29 months
d Cracked circumferentially.

of the thin-walled tubes cracked in the HgNO₃ test and only two specimens of one tube on atmospheric exposure. Most of the medium tubes cracked in HgNO₃ and five individual tubes on exposure. All but one (C-7, whose action is unaccountable) of the thick-walled tubes cracked HgNO₃ and seven failures on exposure were found.

In Fig. 8 the internal circumferential stress and the tendency to season crack as measured by the HgNO₃ test are plotted against the percentage reduction of outside diameter for sunk tubes only. For all three initial sizes the circumferential stress approaches a straight-line function of the diameter reduction. Also, the greater the initial wall thickness, the greater the internal stress. With the thickest wall tubes used and the greatest diameter reduction, stresses as high as 60,000 lb. per sq. in. were found by means of the split-tube method described above. The reciprocal of the time to crack in mercurous nitrate solution, which

is taken to be a measure of the tendency to season crack, also increases as practically a straight-line function of diameter reduction. A somewhat greater tendency to crack is noted with the heavy-walled tubes than with the thin-walled tubes.

The somewhat complicated relations between intensity of stress and tendency to season crack and the type and degree of reduction are shown fairly well in Figs. 9, 10 and 11. In Fig. 9 the data from tubes drawn and sunk from 1 by 0.025 in. are presented. Both the internal stress and the tendency to season crack are sharply reduced with increasing area reduction. It is also quite apparent that for a given area reduction a greater
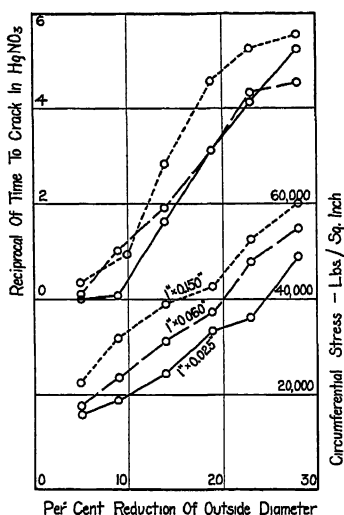
FIG. 8.

FIG. 9.

FIG. 8.—EFFECT OF DEGREE OF SINK ON INTERNAL STRESS AND TENDENCY TO SEASON CRACK IN HIGH-BRASS TUBES.
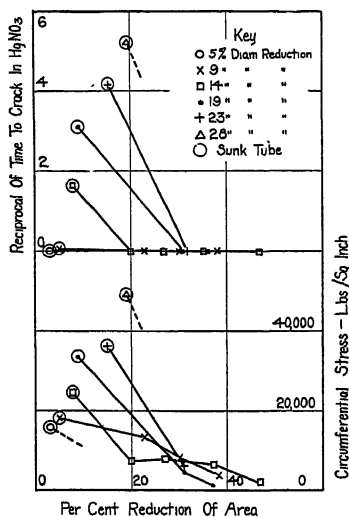
FIG. 9.—EFFECT OF AREA REDUCTION AND DIAMETER REDUCTION ON INTERNAL STRESS AND TENDENCY TO SEASON CRACK IN HIGH-BRASS TUBES DRAWN AND SUNK FROM 1 IN. BY 0.025 IN.

stress and greater tendency to crack are encountered with a relatively large diameter reduction. While, for small diameter reductions, practically any area reduction is safe from the season-cracking standpoint, comparative safety with a larger diameter reduction is only obtained by a reduction of area of from 25 to 30 per cent. In other words, tubes in the range of size noted may be given practically any type of reduction with safety, provided the area reduction is greater than 25 to 30 per cent.

The data presented in Fig. 10 are for tubes drawn and sunk from an initial size of 1 in. outside diameter by 0.060 in. wall thickness. In general, the characteristics shown are similar to those in Fig. 9 for the thinner walled material. While the general form of the curves is the

same, there is one marked distinction with the 0.060-in. material in that the curves are shifted vertically. For this range of tube size, safety with small area reductions can only be obtained when the diameter reduction is small. On the other hand, practically complete immunity to season cracking with any type of reduction is obtained when the area reduction is in the neighborhood of 45 per cent. or greater.
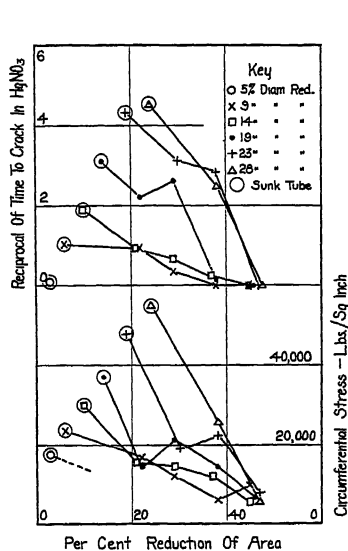
FIG. 10.
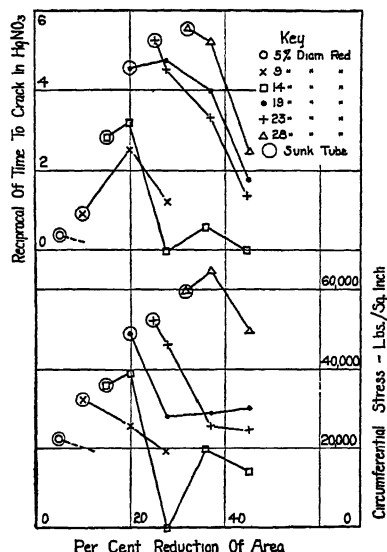
FIG. 11.

FIG. 10.—EFFECT OF AREA REDUCTION AND DIAMETER REDUCTION ON INTERNAL STRESS AND TENDENCY TO SEASON CRACK IN HIGH-BRASS TUBES DRAWN AND SUNK FROM 1 IN. BY 0.060 IN.

FIG. 11.—EFFECT OF AREA REDUCTION AND DIAMETER REDUCTION ON INTERNAL STRESS AND TENDENCY TO SEASON CRACK IN HIGH-BRASS TUBES DRAWN AND SUNK FROM 1 IN. BY 0.150 IN.

In the case of tubes drawn and sunk from an initial size of 1 in. outside diameter by 0.150 in. wall thickness, a still further shifting of the curves vertically is noted in Fig. 11. In general, the curves follow the same form as with the thin and medium-gage tubes already referred to. It should be noted that with tubes of this wall thickness it is difficult but not impossible to obtain a low stress and low tendency to season crack with any type of reduction where the area reduction is small. Even with reductions as high as 45 per cent. in area, all but the best type operations show considerable stress and a marked tendency to season crack. With this range of size, comparative immunity to season cracking as drawn can only be obtained when the area reduction is fairly large (perhaps 35 per cent. or more) and at the same time the diameter reduction is below perhaps 15 per cent.

SUMMARY AND CONCLUSIONS

1. The general split-ring method for evaluating internal stress in tubes is only reliable when rather wide strips (*i. e.*, long sections of tube) are used.

2. The copper content of brass tubes has a profound effect on tendency to season crack. Tubes of 90 per cent. copper or over are practically immune and those over 80 per cent. copper are fairly so. Tubes in the high-brass range are strongly susceptible to season cracking. Tubes of 60 per cent. are decidedly the most susceptible.

3. Iron and lead have no practical effect on season cracking. Lead, however, has a very powerful effect on fire cracking.

4. Tin has a slight but distinctly protective effect on season cracking.

5. The reciprocal of the time in minutes to crack in standard $HgNO_3$ solution is a fairly reliable criterion of the tendency to season crack.

6. The tendency to season crack increases directly with intensity of internal stress. Total immunity is obtained when the circumferential stress by the method used is below approximately 12,000 lb. per sq. inch.

7. In high-brass tubes the intensity of internal stress and the tendency to season crack are:

    A. Increased by

        a. Increase of wall thickness in proportion to diameter

        b. Hollow sinking instead of drawing over a plug

        c. Increase of diameter reduction.

    B. Independent of

        a. Rockwell hardness or other physical properties.

    C. Decreased by

        a. Increasing area reductions.

8. With properly designed drawing operations it is possible to draw practically any size of brass tube to any degree of hardness and have it free of tendency to season crack. The difficulty of accomplishing this, however, increases considerably with very thick-walled tubes. Tubes so drawn obviously do not require relief annealing to be safe from season cracking

DISCUSSION

A. MORRIS, Bridgeport, Conn. (written discussion).—Mr. Crampton has made a real contribution to the existing knowledge of means of measuring internal stress in hard-drawn tubes. His results, however, are directly proportional to the assumed value of modulus of elasticity. We know that certain physical characteristics of drawn brass differ, depending upon whether the test is made with or across the grain. The question in our mind is: How close to the correct value for all mixtures under test is this assumed value of 15,000,000 lb. per square inch?

Mr. Crampton assumes that "since the longitudinal cracks prevail in drawn tubes, these are caused by tangential stresses which must be greater than the longitudinal stresses." We do not believe this is necessarily so. When annealed brass is placed

under tensile stress and subjected to ammoniacal or mercury corrosion, the cracks that develop are always in a plane perpendicular to the direction of the applied stress. (Fig. 12.) The tube shown was subjected to a torsional stress of 100 ft.-lb. The cracks developed are at 45° to the axis of the tube, and are perpendicular to the direction of maximum tensile stress. It is generally recognized that drawn tubes have both longitudinal and circumferential internal stresses. If that is so, the maximum stress is the resultant of these two, both in magnitude and in direction; therefore the cracks might be expected to assume some angle with the axis of the tube, were it not for the presence of some other directional factor. It seems probable that this factor is the longitudinal orientation of the elongated crystals. Season cracking is an intercrystalline phenomenon. In drawn brass the greater portion of the intercrystalline area is longitudinally disposed. Any crack at an angle with the axis of the tube would have to traverse a large number of grains. It would therefore seem that cross cracking can be expected only in cases where the internal stress is almost entirely longitudinal, and then only under severe conditions of selective corrosion.
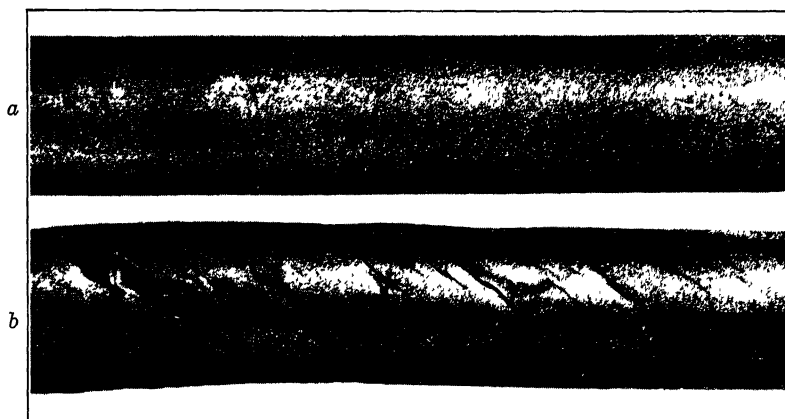
FIG. 12.—TUBES SUBJECTED TO TORSIONAL STRESS OF 100 FT-LB. AND TO AMMONIACAL
CORROSION.
    a. Muntz metal annealed at 500° C. ½ hr. and quenched in water.
    b. About 66 per cent. copper annealed to 0.030-mm. grain size.

Mr. Crampton has used the mercury test as an indication of tendency to season crack. It is fairly well established that most if not all season cracks are caused by stress and ammoniacal corrosion. In service, cracking is caused by intercrystalline attack by ammonia. In the test, cracking is caused by the same preferential attack by metallic mercury. It would seem that ammonia is the logical agent for an accelerated season cracking test. We feel that Mr. Crampton has shown that the mercury test will give an excellent indication of the relative magnitude of circumferential internal stresses in drawn tube. His figures on atmospheric cracking are fragmentary, and we are left in doubt as to whether we can take the further step with him and accept the assumption that the mercury test is a fair indication of the relative tendency to season crack.

In his test of Muntz metal, Mr. Crampton has taken no account of the wide range of physical properties and also the equally wide range of reaction to stress-corrosion cracking that it is possible to produce in a Muntz metal of given composition by heat treatment. In Fig. 12 the uncracked tube is of Muntz metal which has been annealed at 500° C. for ½ hr. and quenched in water. The cracked tube is one of about 66 per

cent. copper annealed to 0.030-mm. grain size.   Both were placed under a torsional stress of 100 ft-lb. and subjected to ammoniacal corrosion.   The high-brass tube cracked as shown in two days   The Muntz metal tube remained apparently uncracked after two weeks.   Whether this relative immunity carries over into the hard brass after such tubes are drawn, we do not know.   But it may, and if it does, it would seem that further work must be done before final conclusions are drawn concerning the relative susceptibility of Muntz metal to season cracking.

Mr. Crampton's data on fire cracking are extremely interesting.   Mill experience has shown that mixtures drawn from a cast shell are much more likely to fire crack than would be the same mixture made from a billet pierced on a Mannesmann machine.

J. L. CHRISTIE, Bridgeport, Conn.—Possibly the following may be the reason why lead is so effective in promoting fire cracking and not the other types of cracking.   We know that a piece of highly stressed brass when emersed in molten solder will frequently fly apart, probably owing to an attack of the metal by the solder as well as to the temperature involved.   Lead does not actually dissolve in brass.   It is present in the form of free lead, and it may be that this free lead has a certain chemical attack on the brass similar to the attack of mercury and of molten solder.

O. W. ELLIS, Toronto, Ont.—Mr. Crampton says, in his Conclusions, "In high-brass tubes the intensity of internal stress and the tendency to season crack are increased by the increase of wall thickness in proportion to diameter, hollow sinking instead of drawing over a plug, and increase of diameter reduction, independent of Rockwell hardness or other physical properties."   In the paper I have not been able to find any reference to physical properties other than Rockwell hardness.   I raise the question as to whether the intensity of internal stress is independent of other physical properties.

In 1915, I had occasion to investigate a large number of brass rods that were in process of season cracking, which had come from various lots of rods received from manufacturers.   I made an experiment somewhat after the following description:

I took a series of test pieces from rods which varied considerably in their mechanical properties, in particular their tensile strength, and made tests on pieces that were cut in the immediate vicinity of the pieces that were formed in the test pieces.   These pieces were slotted along the diameter in a longitudinal direction; we determined the amount by which these slotted pieces opened up after the slot had been made, and we found that within certain limits there was a definite relationship between the tensile strength of bars and the amount by which the slot opened.   When, however, the tensile strength of the bars had reached a certain limiting value, which I am not able to quote at the moment, the relationship between the tensile strength of the bars and the amount by which the slot opened fell by the board altogether.   I wonder whether, in cases where the internal stresses are somewhat less than those that Mr. Crampton has dealt with here, there may not be a definite relationship, if not between Rockwell hardness and internal stress, between tensile strength and internal stress, and I wonder, too, whether even with stresses beyond those where the Rockwell relationship falls down the tensile internal stress relationship may not still exist.

H. A. STAPLES, Elizabeth, N. J. (written discussion).—The writer is not in full accord with the phraseology in the last of Conclusion 8 of Mr. Crampton's paper.   Possibly it is a difference in language   It is our belief that in hard-drawn brass tube the tendency to crack is always present.   It is true that stresses may be balanced so that the tube does not crack, but the tendency to crack is inherent in the material in the stressed condition.

Some twenty-odd years ago the writer made a series of season-crack tests with high brass, starting with 2 per cent. reduction of area by sinking and carrying the

draws all the way up to 30 per cent. The samples drawn only 2 per cent. hard failed when exposed to the air for a period of nine months. This test has been repeated many times with irregular results.

In our experiments, to secure balanced stresses we drew tubes through a die and plug shown in Fig. 13. The plug was made with the same contour as the die, so that by changing the location of the plug relative to the die, we could set up different stresses. To test the tube, we cut slots $\frac{1}{4}$ in. apart, as in Fig. 14, leaving the end of the strip free.

We also cut circles from the same piece, and slotted them as in Fig. 15. We found it possible to balance stresses, so that there would be no change in dimensions of these circles when cut, or to balance them so that the strip in the longitudinal section would not change position when cut free, but under no conditions could we balance the different sets of forces so that both would be normal at the same time. That is the nearest to a balanced stressed tube that we were able to produce.

We have tested tubes that have been given standard draws with the mercurous nitrate solution and have found no signs of stress in them, but when we plugged these same tubes so that the solution was either on the inside or the outside of the tube, with the opposite side not subjected to solution, the tubes showed signs of stress. In service we rarely get corrosive conditions the same on the outside as on the inside, and I want to reiterate the idea I have tried to put across; that there is always a tendency to crack present, and the only safe way to use brass tubes with the common alloys where they are subject to corrosive conditions is to use them

FIG. 13.—DIE AND PLUG.
FIG. 14.—SLOTS CUT IN TUBE FOR TESTING.
FIG. 15.—SLOTTED CIRCLES CUT FROM TUBE FOR TESTING.

with an inert structure secured by relief annealing sufficient to relieve stresses. Complete recrystallization assures this condition.

In paragraph 3 on the first page, where the author has drawn general conclusions, he has made a reference to the percentage of zinc. This is probably generally correct, but I doubt whether it is correct within the range of 60 to 63 per cent. In mill practice we know that tubes within that range are less susceptible to fire cracking both with lead and without lead, and in season cracking we fail to see any material difference between the two alloys within the limits of our ability to measure them.

I certainly concur in his remarks with respect to the addition of tin. A very small percentage of tin will materially increase resistance to corrosion.

E. M. WISE, Bayonne, N. J.—There is another factor that seems to be tacitly assumed here—the assumption that the stress distribution is a linear function of the distance from the neutral axis of the tube. This may or may not be true. I believe that cracks will actually initiate at the surface only when the stress at this point (the surface of the tube) exceeds a definite limiting value. Mr. Staples' discussion hinges around this phenomenon.

If the method employed in drawing the tube is such that high surface tensile stresses are produced, the material will start to crack superficially, and cracks once

started will probably continue to propagate through the material in spite of the fact that the average stress in such a tube may be small.

If a tube is produced by methods that leave residual stresses in the tube distributed as shown in Fig. 16, the methods used by the author in determining the value of the surface stress apply, but if a tube is drawn by methods that leave residual stresses distributed as shown in Fig. 17 the apparent stress in such a tube may be zero in spite of the fact that the surface stress would be very high and the tube would undoubtedly start to crack.
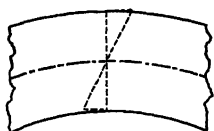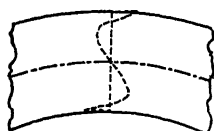
FIG. 16.   FIG. 17.

If the surface of a section of the tube were removed by dissolving, or by other methods, the warpage due to this treatment would be a fair index of the stress in the immediate vicinity of the surface.

J. R. TOWNSEND AND R. L. GERUSO, New York, N. Y. (written discussion).
The author's careful study adds materially to our knowledge on this subject. As a matter of interest it would be fitting to cite an example of season cracking which recently came to our attention. A phosphor-bronze bushing on a rheostat, such as is shown in Fig. 18 failed in service. The arrow in this figure clearly indicates the crack, which penetrated the section. Figs. 19 and 20 show the intercrystalline failure.

Season-cracking failures in the electrical communicative industry have been eliminated in the customary known ways—release of high internal strains either by change in design of parts or more commonly by a low-temperature anneal.

It has also been found that nickel-silver clamping springs, six numbers hard and with an approximate chemical composition of copper, 53.5, nickel, 16.5, zinc, 25.5 per cent. and remainder iron were subject to corrosion cracking. Laboratory tests of nickel silver showed that specimens cut transversely and diagonally were more susceptible to corrosion cracking when subjected to bending than were longitudinally cut specimens. It was further observed that coarse crystalline nickel silver had a very low resistance to corrosion cracking, as measured by the mercurous nitrate immersion test, when subjected to stresses. Cold-working such large-grained material a slight amount (approximately 5 to 10 per cent.) was found to make it more resistant to corrosion cracking. The manner in which the author has evaluated this mercurous nitrate test is commendable, for it is only when comparing a laboratory test with service conditions that a true and reliable comparison may be drawn.

Fig. 20 shows that with increasing width of diametral rings, the apparent internal stress in the material increases, whereas for longitudinal stress, with increasing width, the apparent internal stress decreases. It would be interesting to supplement these experiments in order to determine at what point the apparent internal stresses in each strip, for both methods of test, were equal.

FIG. 18.—SEASON CRACKING FAILURE OF PHOSPHOR-BRONZE BUSHING. NATURAL SIZE.

At the time of reading this paper an article by Fox[5] came to our attention. Fox said that errors occurred in employing either the tongue method of Anderson and

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[5] J. Fox: The Measurement of Initial Stresses in Hard-Drawn Tubes. *Engineering* (1930) 65.

Fahlman[6] or the split-ring method of Hatfield and Thirkell[7] for measuring the internal stresses in hard-drawn tubes. He further stated that the calculation of the maximum internal stress should be based upon the amount of internal couple release and not on any particular stress as is located at the extreme fibers. As the author has stated that "total immunity is obtained when the circumferential stress by the method used is below 12,000 lb. per sq. in.," it would appear that this value (12,000 lb. per sq. in.) is not a true and reliable one. If the greatest stresses imparted are towards the surface, then according to the calculation of the author an extremely high internal stress would

FIG. 19.—INTERCRYSTALLINE FAILURE OF PHOSPHOR-BRONZE BUSHING. × 115.

be induced, whereas the same amount of stress may be irregularly distributed throughout the thickness of the tubes and only a small internal stress determined.

It is gratifying to see that the author has produced experimental evidence to show that lead increases the tendency of brasses to fire crack. Mr. Christie's suggestion that the increasing tendency of brasses containing lead to fire crack is due to its insolubility in brass hardly appears to be the full explanation. It is our belief that the cause for this particular phenomenon is the great difference in thermal expansion of copper $(16.8/°C. × 10^{-6})$ $(0° - 100° C.)$ and lead 27.09 $/°C. × 10^{-6}$ $(25°$ to $100° C.)$ as well as its insolubility in copper. Upon severe cold working large quantities of heat are generated which indirectly induce exceptionally high internal stresses due to the great differences in volume of copper and lead. These high internal stresses seek release and it is not surprising that even a light tap initiates failure.

Investigators differ as to the actual benefits derived from small percentages of tin in brass. Moore and Beckinsale[8] stated that the addition of 1 per cent. of tin to 70/29 brass caused tin to become more sensitive to season cracking. Jonson[9] also stated

[6] R. J. Anderson and E. G. Fahlman: U. S. Bur. Stds. *Tech. Paper* 257 (1924).

[7] W. H. Hatfield and G. L. Thirkell: *Jnl.* Inst. of Metals (1919) **22**, 67–91.

[8] H. Moore and S. Beckinsale: The Removal of Internal Stress in 70:30 Brass by Low Temperature Annealing. *Jnl.* Inst. Metals (1920) **23**, 225–235.

[9] E. Jonson: Failures of Forgible Bars. *Trans.* Amer. Inst. Metals (1914) **8**, 135.

that increasing the amount of tin in brass increases the tendency to season crack. Since this observation has also been recorded by other investigators and is in contradiction to the evidence furnished by the author, it might be well to repeat the experiments of these previous investigators.

The author has used indiscriminately the terms "corrosion cracking" and "season cracking." Season cracking, it appears to us, is a specific term which refers to a failure common to brasses and copper-base alloys, whereas corrosion cracking is a general term applied to all types of failure, regardless of the alloy, which have been caused by corrosion. It would be well to differentiate between these two terms.
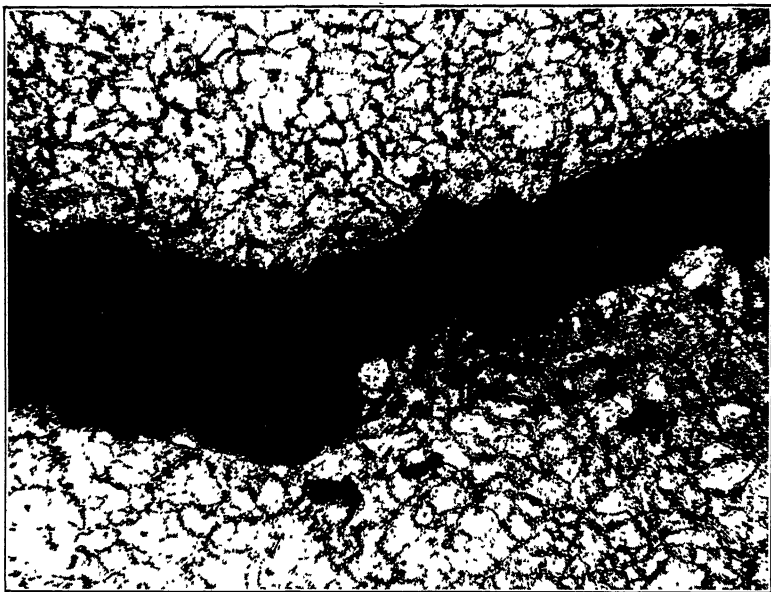
FIG. 20.—INTERCRYSTALLINE FAILURE OF PHOSPHOR-BRONZE BUSHING.   × 300

D. K. CRAMPTON (written discussion).—Mr. Townsend and Mr. Geruso suggest an extension of tests shown in the original Fig. 3, to determine the points at which the apparent internal stresses in diametral rings and in longitudinal strips become equal. This would have no physical significance, as the falling off of the apparent stress in the longitudinal strip is due to the strengthening effect of the transverse curvature of the strip. This was pointed out in the original paper in describing the curves in question.

Their reference to Fox's paper, which was not available at the time of writing of the present paper, is appreciated. In the original paper no claim was made as to distribution of stress through the tube wall and, in fact, it is obvious that with the method used the stress determined is a summation of the stresses at the various points through the wall. They make the suggestion as to high internal stresses due to the difference in coefficients of thermal expansion of copper and lead, and I believe this may have some bearing on the fire cracking, but not in just the way they suggest. If the mechanism were precisely as they postulate, it would mean that there were higher stresses present with a higher lead content and therefore a greater tendency to season crack as determined by the mercurous nitrate test, as well as by fire cracking test. The facts, however, are that the increased lead did not seem to increase tendency to

crack in the mercurous nitrate solution. On the other hand, it markedly increased the tendency to fire crack when rapidly heated. It is felt that therein lies the true explanation. Fire cracking occurs only on very rapid heating and it is possible that with rapid heating the stresses due to the expansion of the lead come into play.

Mr. Morris brings up the question of the propriety of using the assumed value of 15,000,000 lb. per sq. in. for the modulus of elasticity for all alloys used. The only possible place where any difficulty could have resulted from this assumption was in Fig. 6, showing the distribution of stress according to copper content. Even here the error so introduced is small in proportion to the difference shown between the various alloys involved.

Mr. Morris' discussion of the directional distribution of stress and intercrystalline materials is interesting, but the author cannot see that it forms a valid objection to his statement that cracks are due to tangential stresses greater than longitudinal stresses. We know very little about the actual conditions existing at grain boundaries, and if there were a greater amount of intercrystalline material longitudinally disposed, it would seem that this would offer greater resistance to the cracking rather than less.

Mr. Morris also objects to the use of mercurous nitrate as an indication of tendency to season crack, stating that ammonia is the logical agent for accelerated season-cracking tests. In defense of the use of mercury salts, it should be pointed out that almost invariably investigators have used this and with highly satisfactory results. The author has been unable to determine from a study of the literature that concentrated ammonia is any more reliable in this connection than mercurous nitrate. Further, the relative slowness of the ammonia as compared to the mercury would make its normal use prohibitive. While the results reported in the paper as regards correlation of mercury tests and exposure tests are not complete, it is thought that they were sufficiently so to indicate that the mercury test as used is quite reliable.

Mr. Ellis objects to the statement that tendency to season crack is independent of Rockwell hardness or other physical properties. It is a fact that in the paper presented other physical properties were not reported, but it has been found that tensile strengths, etc., do follow closely the Rockwell hardness. However, as pointed out in the paper, the intensity of internal stress varied markedly with the type of reduction, independently of the degree of reduction. The Rockwell hardness and tensile strength follow the degree of reduction very closely, but seem almost entirely independent of the type of reduction. The tests on rod quoted by Mr. Ellis are hardly relevant to this particular point, as there is only one type of reduction available on rod in contrast to the considerable variety in type of reduction in drawing tubes.

Mr. Staples believes that in hard-drawn brass tubes the tendency to crack is always present, and does not therefore agree with the statement in conclusion No. 8 of the paper. It is felt that Mr. Staples could not have studied the paper carefully, as this point was amply and conclusively demonstrated. It was especially well shown in Tables 4 and 5, that tubes of almost any degree of hardness could be obtained with very low internal stresses as drawn, and that these positively could not be cracked in mercurous nitrate solution. In fact, although it was not reported in the paper, the author has seen several examples of tubes drawn in such a way that apparent circumferential stress by the method used was compressive instead of tensile. That being the case, it is inconceivable that a tube would have any tendency to season crack. Mr. Staples quotes some tests. As is pointed out in the paper, the use of such narrow strips leads to entirely erroneous results.

Stress-corrosion Cracking of Annealed Brasses

By Alan Morris,* Bridgeport, Conn.

Season cracking of brass has received wide attention and there is a wealth of technical literature on the subject. Its causes are fairly well understood and means for its prevention are inexpensive and effective, so that the frequency of failures from this source has diminished of recent years. But its sister phenomenon, the failure of annealed brass by reason of applied tensile stress plus a certain type of corrosion, has received less attention, though it has been responsible for occasional more or less troublesome cases of cracking of brass in service. The work described in the following pages was undertaken about two years ago to determine the relative resistance of various commercial brass mixtures to stress-corrosion cracking, and to learn something of the controlling factors. By stress-corrosion cracking we mean the cracking of brass free from internal stresses by reason of applied tensile stress and simultaneous attack by certain corrosive agents.

Rogers,[1] in discussing a paper by Hatfield and Thirkell, says: "He had also applied a solution of mercuric salt to tensile test pieces of brass whilst they were under stress in the testing machine. At very moderate stresses such test pieces cracked, and very readily broke."

Moore, Beckinsale and Mallinson[2] subjected test pieces to simultaneous corrosion and tensile stress. In order to determine the minimum stress detectable in brass by the mercurous nitrate test, tensile samples were placed under stress and treated with mercurous nitrate solution. They found that brass stressed below a minimum did not crack.

Dr. McAdam[3] has investigated the effect of corrosion on the fatigue limit of brasses, among other materials. He directed a stream of either fresh or salt water against the specimen while it was undergoing fatigue test. The corrosion-fatigue limits thus determined may be considerably lower than the endurance limit without coincident corrosion. The exact

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* Research Engineer, Bridgeport Brass Co.

[1] F. Rogers: Discussion on Season Cracking. *Jnl.* Inst. Metals (1919) **22**, 114.

[2] H. Moore, S. B. Beckinsale and C. E. Mallinson: Season Cracking of Brass and Copper Alloys. *Jnl.* Inst. Metals (1921) **25**, 86.

[3] D. J. McAdam, Jr.: Fatigue and Corrosion-fatigue of Metals. Intl. Congress for Testing Materials, Amsterdam, 1927.

relationship, if any, between this form of failure and stress-corrosion cracking has not been determined. In the case of corrosion-fatigue, failure is caused by simultaneous application of repeated stress and corrosion of a general type. The phenomenon is not confined to copper alloys. In stress-corrosion, failure is brought about by static tensile stress and corrosion of a highly special nature. Only certain metals are affected by it. It is to be hoped that future work will throw light on the relation between these two types of failure.

It seems probable that season cracking and applied stress-corrosion cracking are manifestations of the same phenomenon. Moore, Beckinsale and Mallinson have used the term "season cracking" to cover both when they say "Season cracking occurs only in material which is maintained in a state of stress, either by external constraint or more commonly by internal stress." Many of the facts established by investigation of season cracking undoubtedly apply with equal force to both, but it is dangerous to infer too close a similarity in the relative susceptibility of various mixtures to the two types of attack. The tendency of a brass to season-crack under given corrosive conditions is a function of its inherent susceptibility to stress-corrosion attack and also of the magnitude of the internal stresses set up in it by a given cold-working operation. This latter factor probably varies with the physical characteristics of the mixtures. It is conceivable that in two alloys that offer equal resistance to stress-corrosion attack, difference in ductility and elastic properties would cause one to season-crack more readily than the other. Because of this complication and the comparative difficulty of obtaining accurate measurements of internal stresses, it was decided to attack the problem by observing the way in which various mixtures reacted to applied stress plus the proper type of corrosion.

Apparatus Used for Tests

The apparatus used is shown in Fig. 1. It consisted merely of a series of levers by means of which tensile stresses might be applied to a series of samples.

Fig. 2 shows in detail the manner in which each test piece is set up. The lower end passes through a hole in the angle. The nut on the lower end of the piece has a spherical face which sets into a corresponding socket in the angle, making small angular movement of the piece possible. The upper end of the piece passes through a hole in the lever, and through a block of steel so shaped as to provide an obtuse knife-edge rest, which allows for angular movement of the lever. Thus substantially axial loading of the test piece is provided. The angular movement of the lever is always small because the breaks are accompanied by little or no elongation.

The corrosive agent is contained in a glass tube surrounding the shank, closed top and bottom by rubber stoppers through which the
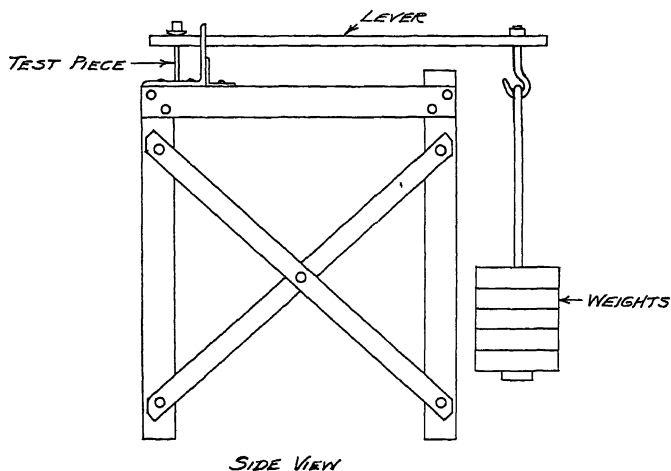
FIG. 1.—APPARATUS FOR APPLYING TENSILE STRESSES.

shank passes. The upper stopper is split for ease of installation, and is pierced by a fine copper tube. The results of preliminary experiments,
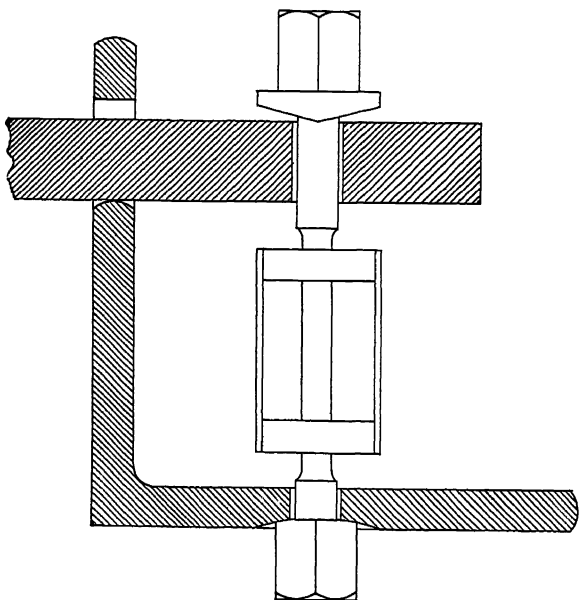
FIG. 2.—TEST PIECE SET UP.

made before the installation of these fine tubes, left something to be desired as to uniformity and reproducibility. After their introduction,

however, results were much better. Their effect may be to equalize pressure, or more probably to allow access of a little air to the corrosion chamber, or both.

CHOICE OF CORROSIVE AGENT

Of the many corrosive agents tried by Moore, Beckinsale and Mallinson[4] they found that only ammonia, ammonium nitrate and mercury would induce season cracking in stressed brass. They detected "ammonia in a water extract of slightly corroded fractures caused by season cracking in brass corroded by atmospheric action only." They concluded that "it is probable that traces of ammonia in the atmosphere are an important agency and possibly the main agency, producing season cracking of stressed brass." They say "it is probable that the behavior of a copper alloy submitted to the combined effect of tension and of ammonia or mercury is a reliable index of its liability to fail by season cracking." Preliminary experiments showed that more concordant results could be obtained by the use of ammonia than were produced by mercury. Accordingly ammonia was chosen for these tests.

TEST PROCEDURE

The test pieces are prepared from ½-in. round rod. A piece 6½ in. long is threaded at each end to take the nuts. A central section 3¼ in. long is turned to ⅜-in. dia. The test pieces are then annealed as desired. All pieces are pickled for 20 sec. in 40.0 per cent. nitric acid and quickly and thoroughly washed just before installation. They are then set up in the testing apparatus and weights are hung on the lever to give the required stress. The ammonia is placed in the tube surrounding the shank of the test piece and the top stopper inserted.

TYPICAL FAILURE

Fig. 3 shows a typical failure produced in the tests reported here. The cracks generally appear on the part of the shank that is within the corrosion chamber, above the level of the liquid. The cracks are always circumferential, lying in a plane perpendicular to the direction of applied stress. Examination of the broken surface shows that the cracks causing failure generally extend inward from the surface about an equal distance at all parts of the circumference.

As the cracks deepen, the stress on the still unattacked portion of the cross-section (upper right corner of Fig. 3) rises, because the load on the specimen remains constant. Failure occurs when this stress reaches a value probably less than the ultimate strength of the material (as shown in

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⁴ H. Moore, S. B. Beckinsale and C. E. Mallinson. *Op. cit.*
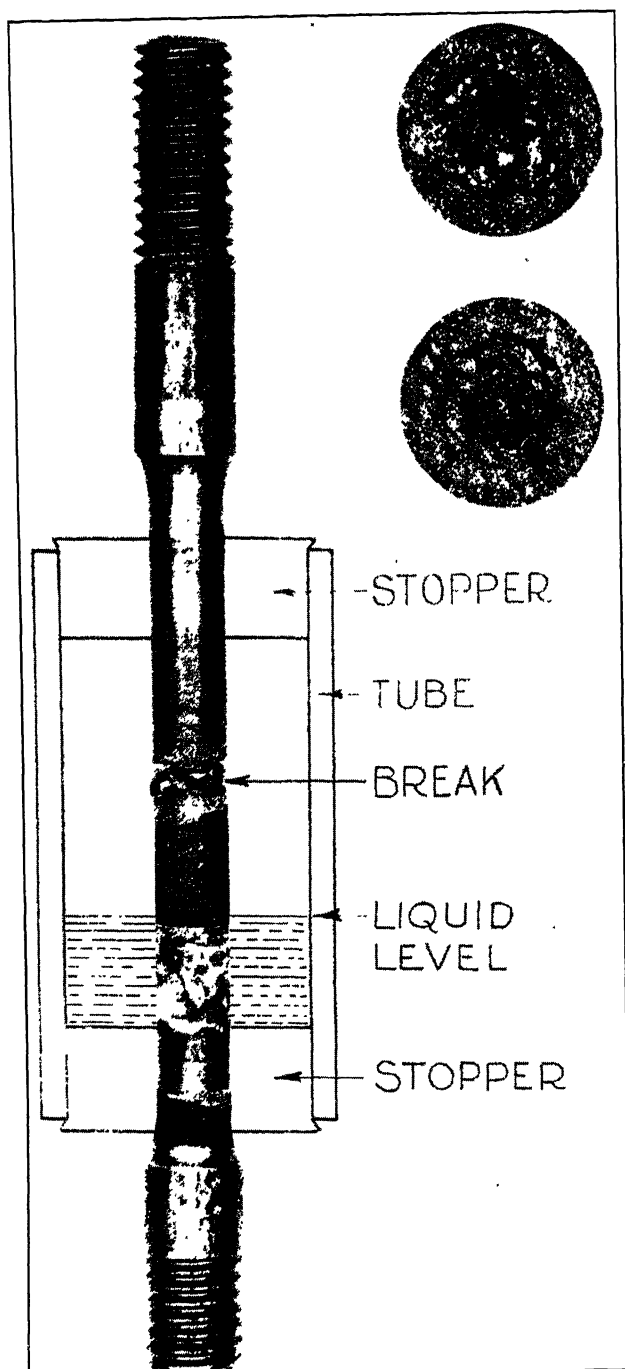
FIG. 3.—TYPICAL FAILURE OF ROUND ROD.   CROSS-SECTIONS IN UPPER RIGHT CORNER.

a tensile testing machine) by an amount of which the magnitude is determined by the stress-concentrating effect of the stress-corrosion cracks.

In the case of soft ductile annealed brasses, this effect is probably not large. In order to test this point, samples showing circumferential marks were tested under the same conditions as some that had been rubbed longitudinally with emery paper. No difference in their behavior was noted; neither could it be seen that the cracks followed the tool marks.

TYPICAL STRESS-TIME CURVE

The method adopted for studying the reaction of any particular alloy was to prepare a number of samples as nearly identical as possible in shape and structure. These were set up under various stresses, time before failure being noted. When stress as ordinate is plotted against time before failure as absissa on ordinary cartesian coordinate paper, the resulting curve slopes steeply downward from the left, flattens out and seems to approach a horizontal. When the same data are plotted on semilog paper, the curve becomes a series of straight lines (within the range of stresses used), not like the usual stress-cycle curve of the fatigue test. The curve descends steeply to a stress at or near the yield point of the material. Here it changes direction abruptly, proceeding as a straight line of lesser slope, which continues downward to a stress below which the material does not fail by stress-corrosion, at least within the time the samples were kept under test in this work.

All curves shown here are plotted on ordinary cartesian coordinate paper, as the author feels that in this form a truer sense of the relation is imparted. He does not believe that the horizontal approached by the curve is necessarily a safe working stress for the material, though this may prove to be the case. In service failures other factors may enter, such as intermittent loading, vibration and temperature change. In this work the curves are used only to compare resistances of materials differing in analysis and structure.

CALCULATED AVERAGE RATE OF LINEAR PENETRATION

In all of these tests, the size of the specimen and the corrosive conditions have been kept constant. Mixture, stress and structure are the independent variables. In all cases time before failure is the dependent variable noted. Our object is to compare the resistance of the various samples to stress-corrosion attack by comparing the breaking times under like conditions of stress and corrosion. But breaking time will be a measure of resistance only when the samples in question have approximately equal tensile strength. Imagine two materials of different

tensile strength, which would be attacked with equal rapidity. The material of higher tensile strength would hold up longer under like conditions of stress and corrosion, and appear to resist the action better than the weaker one, if time only were used as the criterion.

In order to arrive at a basis of comparison independent of tensile strength, recourse is had to the calculation of the average rate of linear penetration of the stress-corrosion cracks. Knowing the ultimate strength of the material and the applied load, the unattacked section at the moment of breaking can be calculated, then the diameter of that unattacked section, then the depth of attack. Knowing the depth of attack and the time before rupture, the average rate of linear penetration can be calculated. All these operations are simplified into the following formula:

$$p = \frac{D}{2} - \sqrt{\frac{SA}{\pi U}}$$

where

p = linear depth of penetration before failure, inches,
D = original diameter of test pieces, inches,
S = applied stress, pounds per square inch,
A = original cross-sectional area of test piece, square inches,
U = ultimate tensile strength of material, pounds per square inch.

The average rate of linear penetration in inches per hour is $\frac{p}{T}$ where T is the observed time before failure, in hours.

This method assumes that the stress-concentration effect of the cracks is constant in all samples under test, and that omission of this factor from the calculations would affect all results equally. The resulting calculated data then become indices of the relative resistance of the samples to stress-corrosion cracking. As previously stated, the stress-concentration factor in the case of annealed brasses is probably not large. An effort was made to measure the unattacked areas of a number of broken samples. The boundary lines were so indistinct, however, that the accuracy of the measurements was low and therefore of little use in determinimg how the calculated values checked with the experimental results.

The other assumption is that the cracks causing failure penetrate with equal speed from all points on the periphery and that the unattacked section that finally breaks in tension is circular and concentric with the original section. Examination of a number of broken samples indicates that this is roughly true in most cases.

Whether or not we are prepared to accept these assumptions as wholly reasonable, at least the values so calculated may be regarded

temporarily as index numbers representative of the relative resistance of the samples.

EFFECT OF VARIATION OF GRAIN SIZE IN ALPHA BRASSES

The material chosen for this determination was a 65:35 brass containing: Cu, 65.1 per cent.; Sn, none; Pb, 0.03 per cent.; Fe, 0.01 per cent.; Zn, remainder.

Pairs of samples were annealed at various temperatures. One of each pair was given a regular tensile test; the other was subjected to a stress of 9500 lb. per sq. in. and to the action of ammonia, the time
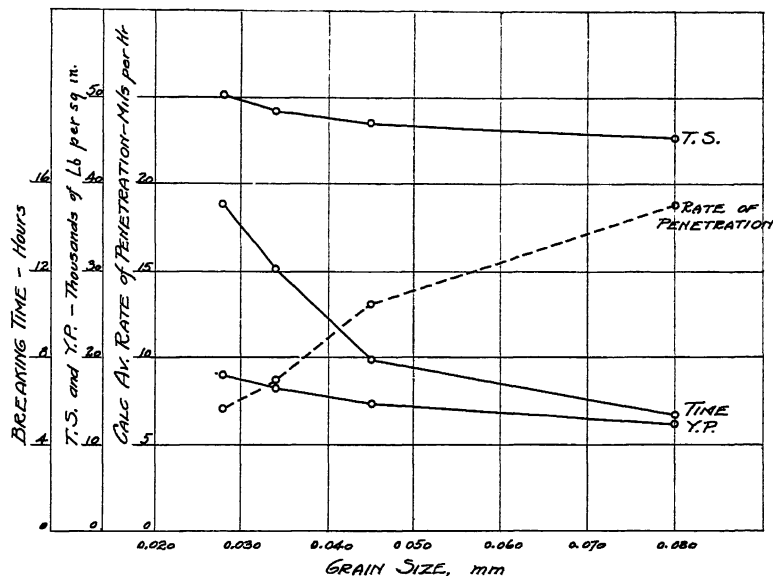
FIG. 4.—TIME BEFORE FAILURE, YIELD POINT AND ULTIMATE STRENGTH PLOTTED AGAINST GRAIN SIZE.

required for failure being noted. Time before failure, yield point and ultimate strength were plotted directly against grain size (Fig. 4).

These curves show that increase in grain size is accompanied by a decrease in the time before failure and, of course, by a decrease in tensile strength and yield point.

The curve obtained by plotting the calculated average rate of linear penetration, as discussed in the preceding paragraph, indicates that the drop in the time curve is more rapid than is accounted for by the drop in the tensile strength curve. In other words, increase in grain size tends to lower the resistance of this mixture to stress-corrosion attack.

The shape of the time curve in Fig. 4 can be made to vary widely, depending on the stress used. If complete stress-time curves correspond-

ing to various grain sizes were prepared, there would be a series of curves, one above the other and approaching one another at the left-hand or steep end. In Fig. 4 the points where the horizontal line representing the stress cuts each of these curves are determined. If a higher stress had been used, the curve would be flatter and lower; with a lower stress, the curve would have risen more steeply toward the left and been generally higher. This same principle applies to Fig. 7.

In order to ascertain more definitely the effect of varying grain size in a high-brass mixture, stress-time curves were determined on two sets of samples taken from high-brass stock, annealed to give a relatively fine
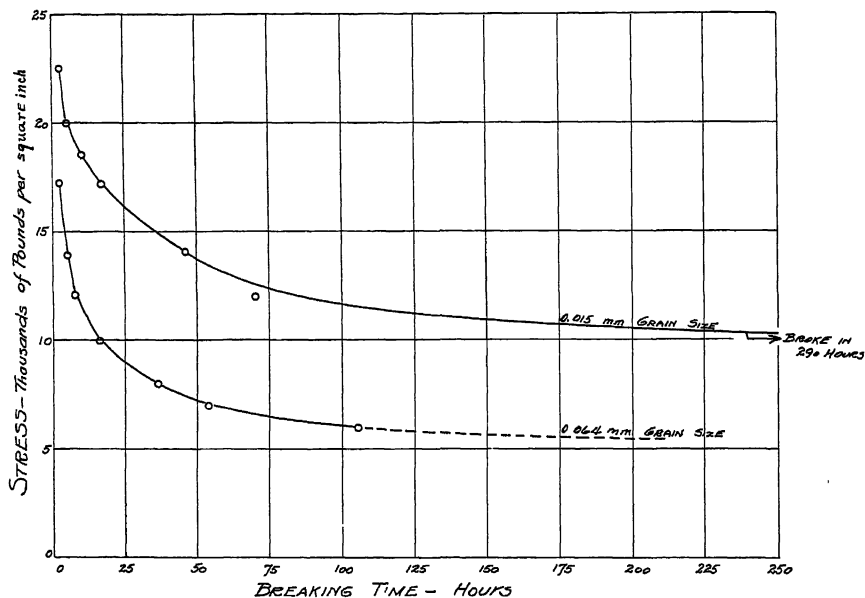
FIG. 5.—STRESS-TIME CURVES OF FINE-GRAINED AND COARSE-GRAINED HIGH-BRASS STOCK.

grain in one set and a relatively coarse grain in the other. The material had the following composition: Cu, 66.4 per cent.; Sn, none; Pb, 0.58 per cent.; Fe, 0.03 per cent.; Zn, remainder. One set of samples was annealed at 500° C. for $\frac{1}{2}$ hr., giving a grain size of 0.015 mm. and a tensile strength of 53,700 lb. per sq. in. The other set was annealed at 650° C. for $\frac{1}{2}$ hr., giving a grain size of 0.064 mm. and a tensile strength of 46,100 lb. per sq. in. The stress-time curves obtained from these two sets are shown in Fig. 5.

Effect of Adding Lead and Tin to an Alpha Brass Mixture

The compositions, grain sizes and tensile strengths of the materials used for these tests are shown in Table 1. The materials were hard

drawn, and the samples were annealed. Samples were set up under various stresses and subjected simultaneously to ammoniacal corrosion, time elapsing before failure being noted in each case.

TABLE. 1.—*Effect of Lead and Tin in Alpha Brass Mixture*

Material	Cu Per Cent.	Sn Per Cent.	Pb Per Cent.	Fe Per Cent.	Zn Per Cent.	Grain Size, Mm.	Tensile Strength, Lb. per Sq. In.
Copper-zinc.....	69.20	nil	0.064	0.035	remainder	0.033	49,200
Copper-zinc-lead	69.42	nil	0 79	0.030	remainder	0 031	47,700
Copper-zinc-tin..	71.67	1.04	0 055	0 016	remainder	0 035	49,500

The samples of the three mixtures are so nearly alike in tensile strength that the positions of their stress-time curves may be taken as an index of their relative resistance to stress-corrosion cracking. The results of these tests are plotted in Fig. 6.
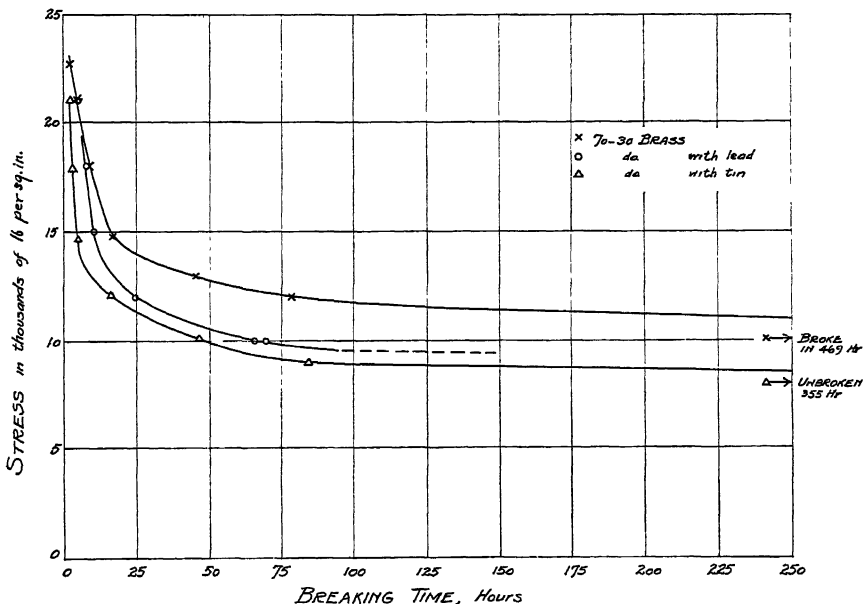
FIG. 6.—STRESS-TIME CURVES OF SAMPLES SUBJECTED SIMULTANEOUSLY TO TENSILE STRESS AND AMMONIACAL CORROSION.

It would appear that both lead and tin lower somewhat the resistance of alpha brass of the 70:30 type to stress-corrosion attack. Perhaps the most important mixture variable is copper. Some work has been done to determine how resistance to stress-corrosion cracking varies with copper content. The data are not yet complete, however.

EFFECT OF STRUCTURE ON RESISTANCE OF ALPHA-BETA BRASS

The first few exploratory tests made with brass of the Muntz metal type indicated that its structure affected its resistance to a marked degree.   The material used was of the following composition: Cu, 60.85 per cent.; Sn, 0.08; Pb, 0.28; Fe, 0.036; Zn, remainder.   The first reconnaissance test consisted of heating pairs of cold-worked samples to temperatures high enough to produce a large amount of beta, quenching one of each pair in water and allowing the other to cool slowly in the furnace. When these pairs were tested under similar conditions of stress and cor-
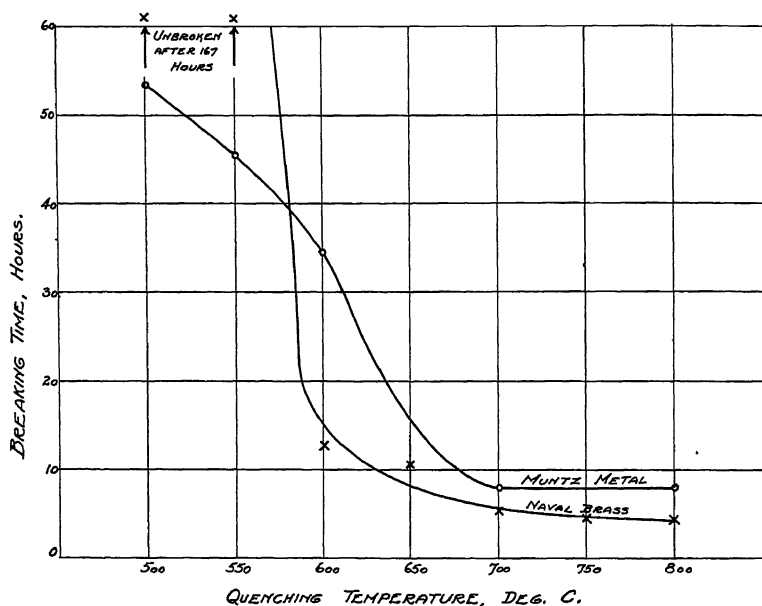
FIG. 7.—STRESS-TIME CURVES OF QUENCHED SAMPLES SUBJECTED TO AMMONIACAL CORROSION.

rosion, it was found that in each case the quenched sample outlasted the slowly cooled one.   It is interesting to note that miscroscopic examination in each case showed that the slowly cooled sample that had failed most rapidly contained more alpha than the corresponding quenched sample, but that this alpha was of the familiar lamellar form taken by alpha that is reprecipitated from beta during slow cooling.

As we were interested in determining how to bring about the highest possible resistance to stress-corrosion cracking, and as the first few exploratory tests indicated that quenching increased resistance, samples were quenched from various temperatures ranging from 500° to 800° C. They were then subjected to a stress of 14,700 lb. per sq. in. and to ammoniacal corrosion.   The time before failure is shown in Fig. 7, plotted

against the quenching temperature. This curve indicates that of the temperatures tried the one quenched from 500° C. showed the greatest resistance.

Two sets of samples were then prepared, one being quenched from 500° C., the other being air-cooled from the same temperature. The quenched samples had a tensile strength of 58,850 lb. per sq. in. The strength of the air-cooled samples was a little lower, that is, 55,900 lb. per sq. in. Complete stress-time curves were determined for these two sets (Fig. 8).
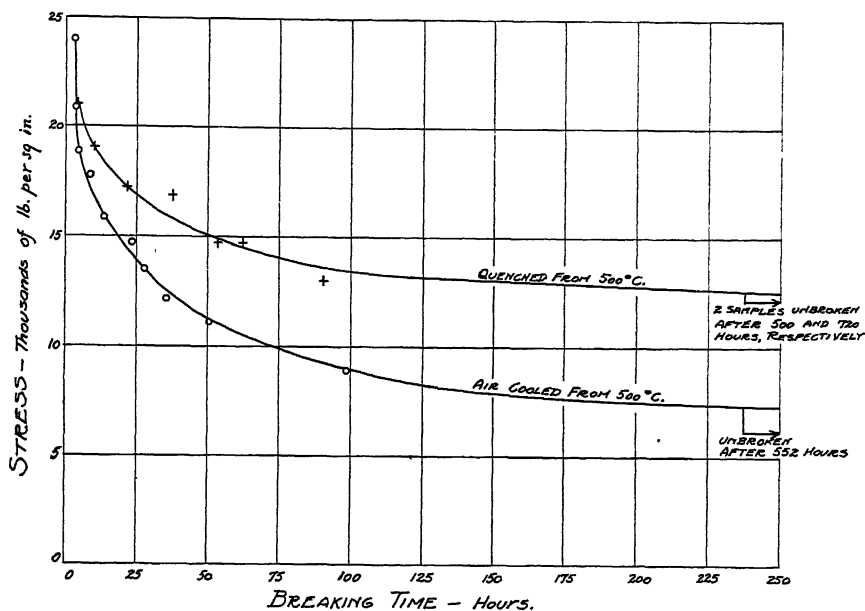
FIG. 8.—STRESS-TIME CURVES OF QUENCHED AND AIR-COOLED SAMPLES.

Samples were prepared from a naval brass of the following composition: Cu, 60.28 per cent.; Sn, 0.75; Pb, 0.11; Fe, 0.016; Zn, remainder. Samples were held at various temperatures ranging from 500° to 800° C. for ½ hr. and quenched in water. They were then subjected to stress of 14,700 lb. per sq. in. and to ammoniacal corrosion. The time before failure in each case was plotted against the quenching temperature (Fig. 7).

Samples of this mixture were heated to 500° C. and quenched in water, and a stress-time curve was determined (Fig. 9). The tensile strength of these samples was 66,400 lb. per sq. in. Comparison of this curve with the curve for quenched Muntz metal shown in Fig. 8 shows that this mixture developed a higher resistance than did the Muntz metal.

Other samples were made up from another lot of raw material of nearly the same analysis as the preceding; *i. e.*, Cu, 59.45 per cent.; Sn, 0.73; Pb, 0.078; Fe, 0.017; Zn, remainder. Samples of this material were heated for $\frac{1}{2}$ hr. at 500° C. and allowed to cool freely in air. Their tensile strength was 64,000 lb. per sq. in. (Lower curve in Fig. 9.)
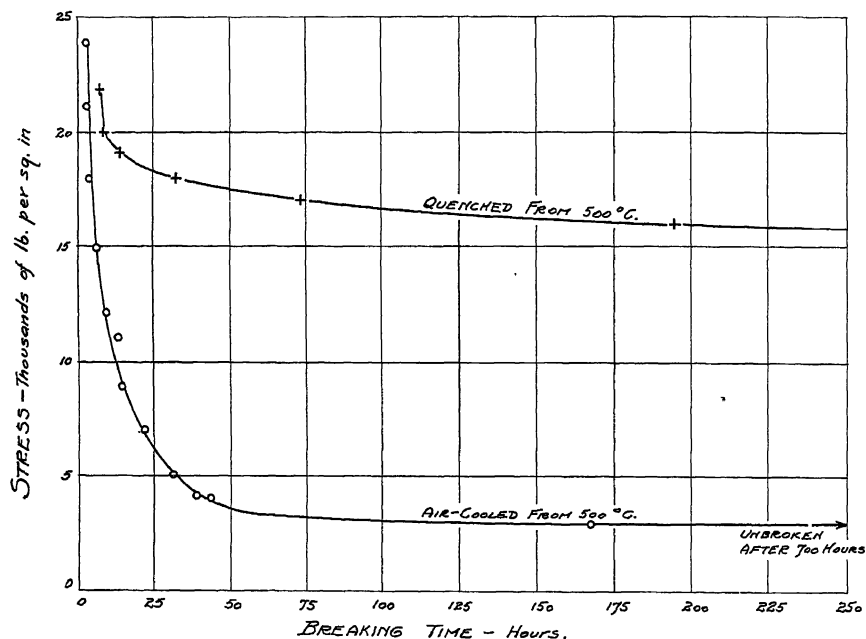
FIG. 9.—STRESS-TIME CURVES OF QUENCHED AND AIR-COOLED SAMPLES OF NAVAL BRASS.

SUMMARY

1. Coarse grain in so-called "high brasses" appears to lower the resistance of the piece to stress-corrosion attack.

2. Lead and tin in an alpha brass tend also to make the material a little less resistant to this form of attack.

3. The resistance of a Muntz metal, and naval brass (and probably of manganese bronze), is materially increased by quenching from a reasonably low annealing temperature.

The writer does not feel that these tests constitute more than a general reconnaissance of the field. The results are presented in the hope that their discussion will hold suggestions that will serve as a guide to further work of this nature.

DISCUSSION

W. B. PRICE, Waterbury, Conn. (written discussion).—Mr. Morris's paper indicates that the stress-corrosion cracking of annealed brasses are manifestations of the same phenomena as season or corrosion cracking and fire cracking.

A case of stress-corrosion cracking recently came to the attention of the writer. Certain-pipe reducing couplings cracked in service. These couplings were turned from high-speed rod and were nickel plated. When unassembled couplings were taken from stock and submitted to a mercury test, they did not crack. If such couplings were assembled by hand and then given the mercury test, they often cracked. Even if the couplings were annealed before assembling, many cracks were encountered after the mercury test. In assembling the fittings for these tests, an excessive wrench pressure was used to get extreme conditions. In practically every case, the pipe nipples were threaded into the coupling up to the shoulder (so that no threads of the nipple were visible below the fitting), which is, of course, bad practice.

In order to determine the effect of wrench pressure on the tendency to season crack, fittings were assembled in a special twist-test machine, capable of measuring the torque (Fig. 10). The alloys shown in Table 2 were used. The results are given in Table 3.
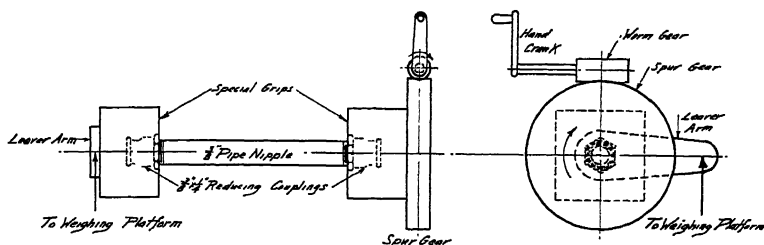
FIG. 10.—TWIST-TEST MACHINE.

TABLE 2.—*Nominal Composition of Alloys Used*

Alloy	Copper Per Cent.	Lead Per Cent.	Nickel Per Cent	Zinc Per Cent.
A (high-speed rod)	61	2.75	0	36.25
B (common leaded brass)....	64	1.00	0	35 00
C (Scovill hardware bronze).............	89	2 00	1	8.00

Alloy C was developed by the writer several years ago for the hardware trade. Such an alloy must have the proper color, be capable of being broached, drilled and tapped on high-speed automatic machines.

It was found that the fittings assembled with a maximum torque of 20 ft.-lb. or less never cracked while those assembled with a maximum torque of 30 ft.-lb. or more always cracked in the mercury solution. Annealing the couplings gave only a slight improvement, for occasional failures were still encountered in assemblies made up with 30 ft.-lb. torque while those assembled with 40 ft.-lb. torque always cracked. A relief heat treatment at 275° C. before assembling was absolutely without effect, for this heat treatment is useful in relieving internal strains only. External strains set up in assembling are not affected, of course, by a prior heat treatment that does not increase the ductility of the metal.

It is my opinion that assembling torques of over 20 ft.-lb. are excessive and should not be used because they usually force the pipe into the fittings to the shoulder (*i. e.*, leave no threads visible below the fitting). With assembling torques of over 30 ft.-lb. the threaded ends of the brass pipe are contracted by the fittings so as to form an

obstruction to uniform flow through the pipes.   Artisans who have been accustomed to assembling couplings and pipe made from wrought iron or steel naturally will use excessive pressure on brass unless properly instructed.

Tests were made on couplings turned from alloy B rod but the fittings when assembled failed in the mercury test, just as readily as those made from alloy A. However, couplings turned from alloy C rod were found to stand up in the mercury solution regardless of the torque used in assembling them; even with 50 ft.-lb. assembling torque, they did not crack.
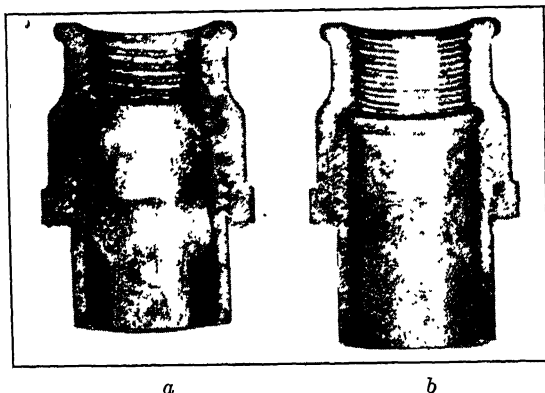
a   b
FIG. 11.—REDUCING COUPLINGS.
a. Alloy C assembled with 40 ft.-lb. torque.
b. Alloy A assembled with 20 ft.-lb. torque.

TABLE 3.—*Results of Tests on Assembled Fittings*

Alloy	Condition	Assembly Torque, Ft.-lb.	Condition of Couplings After 15 Minutes in Mercury Solution
A	Hard	21	O.K.
A	Annealed	21	O.K.
A	Hard	23	O.K.
A	Annealed	23	O.K.
A	Hard	31	Cracked
A	Annealed	31	O.K.
A	Annealed	31	Cracked
A	Hard	42	Cracked
A	Annealed	42	Cracked
A	Hard	52	Cracked
A	Annealed	52	Cracked
A	Hard	56	Cracked
A	Annealed	62	Cracked
B	Hard	20	O.K.
B	Hard	30	Cracked
B	Hard	40	Cracked
B	Hard	50	Cracked
C	Hard	20	O.K.
C	Hard	30	O.K.
C	Hard	40	O.K.
C	Hard	50	O.K.

Table 3 indicates that couplings made from alloy C are foolproof and will not season crack, no matter how badly they are abused in assembling.

Fig. 11 shows a reducing coupling made from alloy C, assembled with a torque of 40 ft.-lb. Note how the threaded ends of the pipe are contracted, and also the break in the threads on both the coupling and the pipe. It also shows a reducing coupling made from alloy A, assembled with a torque of 20 ft.-lb. There is no break in the threads or contraction of the threaded portion of the pipe.

In these tests none of the pipes cracked, probably on account of the external compressive stress set up by the coupling. There have been numerous cases, however, where fully annealed pipe has stress-corrosion cracked in service on account of external circumferential and tangential stresses set up by faulty assembling. In such cases the consumer always assumes that the producer is at fault, when the failure is really due to faulty installation.

This is another example of the necessity of using the proper alloy for the job, and further points out the fact that high-copper alloys are not susceptible to season cracking or stress-corrosion cracking.

H. A. BEDWORTH, Waterbury, Conn.—Mr. Price's discussion has brought out an important point; namely, that alloys high in copper content are not susceptible to season cracking in ordinary service or in the mercury test. That is, experience has shown that alloys containing over roughly 75 per cent. copper are not liable to season cracking under ordinary conditions of service.

D. J. McADAM, Jr., Annapolis, Md.—This paper is of considerable interest to me because I have been doing work on the effect of cyclic stress on corrosion and this paper describes the effect of steady stress on corrosion. There is much need for work to connect the effect of steady stress and the effect of cyclic stress. It would be of interest if Mr. Morris (as he probably intends doing) would try the effect of relieving the stress at intervals.

In experiments that I described last year[5] the effect of repeatedly applying and releasing the stress was shown to be surprisingly great. Applying and releasing the stress once an hour has considerable effect. Later experiments have shown that applying and releasing the stress at even longer intervals has appreciable effect. It seems probable that there is a close connection between the effect of steady stress and the effect of cyclic stress on corrosion.

H. S. RAWDON, Washington, D. C. (written discussion).—The behavior of metals under the simultaneous action of corrosion and stress is, in the opinion of the speaker one of the most important subjects falling within the field of activity of the physical, metallurgist. It is also one of the most fascinating subjects he is called upon to study. A case that came under observation of the speaker several years ago would appear to have a direct bearing on the subject now under discussion.

The heads of several Naval brass bolts ($\frac{7}{8}$ in. dia.) which had dropped off in service were received for examination. The bolts had been used in marine service and corrosion was immediately suspected of contributing to the failure, if not of being the sole cause. The appearance of the fractured face of the bolt head is shown in Fig. 12a. The characteristic features were a central crystalline area $(x - x)$ surrounded by a smooth area $(x - x')$, roughly annular in shape, which in appearance was rather suggestive of the "detail" portion of a fatigue fracture. This appearance is similar to that shown by Mr. Morris in his Fig. 3. An examination of the microstructure of the material immediately adjacent to the face of the fracture revealed some interesting features. The brass was of the α-β type and in the central area there was nothing

[5] D. J. McAdam, Jr.: Corrosion of Metals as Affected by Stress, Time and Number of Cycles. *Trans* A. I. M. E., Inst. Met. Div. (1929) 56.

unusual observed as to the relationship between microstructure and fracture. The path of the fracture was found to show no preference for following either the α or β constituent, but crossed α and β areas indiscriminately, as is the case when a specimen of this material is broken in the ordinary manner in tension. In the smoother area surrounding the rougher central portion, a distinct relationship between the path of the fracture and the microstructure was observed (Fig. 12b). The β areas in that portion of the metal immediately adjacent to the fracture were dezincified. The dezincification had extended into the body of the bolt head only to be a very slight depth—about 0.002 inch.
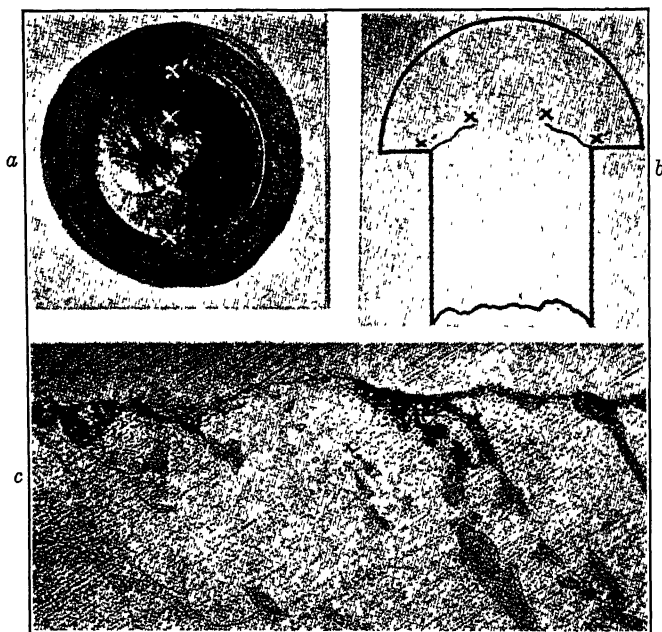
FIG. 12.—STRUCTURE OF α-β BRASS BOLT WHICH FAILED IN SERVICE BY STRESS-CORROSION.

a. Fractured face of bolt head, exposed to sea water, which dropped off in service "of its own accord." × 1.

b. Microstructure of bolt head (× 250) immediately adjacent to the fracture in the smooth annular portion of the break (x' − x). Note the dezincification along the face of the fracture. This was not found in the central portion, x − x, of the fractured face.

c. Longitudinal section of bolt just before head was detached.

The way in which the break most probably occurred is illustrated in Fig. 12c, which represents a longitudinal section of the bolt through the head immediately prior to the detaching of the head. Evidently the break resulted from the combined effect of corrosion and tensile stress. In the sharp angle at the junction of head and shank, the stress was considerably greater than the average stress for the bolt as a whole when the nut was tightened into place. As a result of the relatively high stress imposed on the material, corrosion of the β constituent of the brass was accelerated in this portion of the bolt and manifested itself as dezincification. The circumferential path followed, as the stress-corrosion effect continued, is illustrated in Fig. 12c by x − x', which also corresponds to the annular area marked with the same letters in

Fig. 12a. As the stress-corrosion effect continued, the effective cross-sectional area of the bolt became smaller, until finally the bolt broke as a result of the tensile load it was carrying.

Dezincification of brass is not necessarily to be considered as always accompanying the stress-corrosion of brass. In the case of chloride corrosion of brass of the α-β type, dezincification is probably the general rule. The nature of the corrodent must always be considered, however.

A rather characteristic feature of stress-corrosion of brass, particularly of the α type, is the intercrystalline nature of the fracture that results. It would be interesting to know whether observations on the microstructure of the cracked tension bars were carried out by the author, and whether any obvious relationship between microstructure and path of fracture was observed.

C. G. FINK, New York, N. Y.—Did the breaks invariably occur in the ammonia gas or did some occur in the ammonia solution? I would like to take exception to Mr. Bedworth's statement. He said that brasses with more than 75 per cent. copper do not show this corrosion effect, whereas I believe it is pretty well known that any strained metal is anodic to the unstrained or annealed. Perhaps Mr. Bedworth ought to say that in brasses with more than 75 per cent. copper the tendency to develop the strain-corrosion is decidedly less marked but it is still there, because no matter what the alloy, if it is strained it is less noble than the annealed alloy. It is annolic, as we say, to the annealed alloy.

H. A. BEDWORTH.— I quite agree with Dr. Fink. Practically any metal or alloy will crack if the strain and corrosion are carried to extremes. I had reference to alloys under usual conditions of service, and in those of higher copper content the relative corrosion cranking is so much less than in those higher in zinc or lower in copper that there is a decided line of demarcation.

T. S. FULLER, Schenectady, N. Y.—Having in mind Mr. Rawdon's point, I should like to ask what relation, if any, exists between dezincification and season cracking.

W. R. WEBSTER, Bridgeport, Conn.—Just to get this matter of the liability of season cracking straight, we were asked to furnish some material which was to be employed in an atmosphere that was known as highly corrosive—namely, locomotive smoke. The specifications could only be met by having the material moderately hard drawn. After consideration we decided that if we used a 90 per cent. copper and 10 per cent. zinc mixture we would be safe, and accordingly we filled the order with that material. However, inside of two years, the entire structure came down. Every single piece was season cracked from one end to the other. Some ten or fifteen thousand pounds was involved, so that it was not a question of an occasional crack. Every bit of it let go. That was in 1910.

W. H. BASSETT, Waterbury, Conn.—I have seen copper season crack. We have had some good examples of such cracked copper. I think what we might say about the whole subject is just what Dr. Fink said—that any metal under certain conditions will season crack. From the practical or commercial standpoint, the brasses high in copper and low in zinc are much less liable to season cracking than those which contain a higher percentage of zinc.

It has been our observation that there is a certain relation between dezincification and season cracking. We are not able to make an exact statement but generally speaking the brasses which dezincify or are subject to selective solution will season crack under what we might call ordinary conditions or atmospheric conditions. Those that are not subject to selective corrosion are much less liable to such cracking.

R. L. GERUSO, New York, N. Y.—Does cold working prior to annealing have any effect upon the susceptibility of a brass to season crack?

D. K. CRAMPTON, Waterbury, Conn.—This paper goes into a phase of the subject which has not been fully covered heretofore. I would like to ask Mr. Morris a question in regard to the rather long-time ammonia tests. Some of these tests, I know, ran up into several hundred hours duration. Were precautions taken to avoid any depletion of the solution due to volatility? It is conceivable, after the ammonia has been in the test tube for a considerable number of hours, that it will lose its strength not only by virtue of its reaction but also by virtue of the volatilization of the ammonia.

One other point that I might bring out is the effect of tin and lead. Mr. Morris's work seems to show that both tin and lead have a somewhat harmful influence. The work we have done from an entirely different standpoint, which may not be strictly comparable (although offhand it would seem that both the internal and external stress ought to work about the same) shows that the influence of lead on season cracking is relatively unimportant, although it is highly important on fire cracking, but we found tin rather protective than otherwise.

A. MORRIS.—Dr. McAdam has mentioned the effect of intermittent loading on stress-corrosion cracking. Not only intermittent loading but any change in load seems to have an accelerating effect.

Dr. Rawdon raised the point of the relation between dezincification and stress-corrosion cracking. He shows (Fig. 12) a bolt with a sharp angle between the head and body, meaning that when the bolt was in service there was a high concentration of stress at the corner. That would be the logical place for a stress-corrosion crack to form. It would have taken some time for the crack to spread to a point where the bolt would give way, and in the meantime we might have what Dr. Evans would call a differential aeration cell. There would be a greater concentration of air about the outer portions than in the crack. Probably some rain water or condensed moisture would find its way into the crack already formed by stress-corrosion. The conditions would then be right for dezincification in the crack.

Bolts of this sort are often made of Naval brass or Muntz metal, possibly so heated in forging as to produce a very unfavorable structure. I would rather believe that the occurrence of dezincification in the crack is due to independent corrosive action than that the dezincification had any causal connection with the stress-corrosion cracking.

Many of the fractured test bars have been examined microscopically. In general, the cracks apparently were not as wholly confined to the intercrystalline planes as seems to be the case with the season cracks commonly encountered. The cracks in the alpha-beta test pieces did not seem to favor either constituent particularly.

Professor Fink asked if the breaks ever came below the surface of the liquid. My answer is no. The only times we have produced breaks below the surface level were when the breaks came immediately below the bottom stopper where some of the liquid had seeped down around the shank.

It seems that there are four conditions favorable to rapid stress-corrosion cracking: (1) tensile stress, (2) ammonia, (3) oxygen and (4) moisture. When we began these tests, our breaks always came just below the upper stopper. At first I thought that the accelerating effect at that point had something to do with chemical compounds in the rubber of the upper stopper. I tried everything I could think of that might have been present in the rubber, but nothing seemed to have the desired effect. It then occurred to us that the air diffusing in between the stopper and the shank might come in contact at that point with the ammonia and bring about the observed accelerating effect. The insertion of a fine copper tube through the upper stopper was the remedy. The cracks immediately began to come on that part of the shank above the liquid and below the upper stopper.

At one time we tested some of the higher copper mixtures. In these tests all the breaks came in the upper part of the meniscus.

C. G. FINK.—Where the oxygen concentration is a maximum?

A. MORRIS.—Perhaps, or near the three-phase line. After the test had run for some time, a groove formed below the surface of the liquid, but the cracks did not form in that groove, although that is where one might expect them, on account of stress-concentration. We found the cracks above the grooves in the upper portion of the meniscus. I tried to protect that part of the shank by painting it with a bituminous paint, or covering it with wax up to a higher level. The cracks always formed where the paint left off. We have not yet determined just how to make these tests.

Mr. Fuller raises the question of the general occurrence of dezincification and stress-corrosion cracking at the same time. It has never been our experience. We have never observed a case such as Dr. Rawdon has described, as far as I know. It may be roughly true that brasses that are most susceptible to season cracking also happen to be most readily dezincified. But I know of no definite evidence that there is a causal relation between dezincification and stress-corrosion or season cracking.

Mr. Geruso asked about the effect of cold work prior to annealing. That is a phase that we have not investigated. Beyond what little is known of the effect of previous draws and anneals on the final structure and physical properties of brasses, I do not believe I can offer any experience.

Mr. Crampton mentioned the possibility of the depletion of the ammonia solution during a long-time test. I wish he might have been with us when these long-time tests were taken apart. No quantitative determination has been made, but even after a matter of weeks the ammonia is still very strong, despite the little tubes through the upper stoppers.

Regarding the effect of lead and tin, it seems to me that some further work of correlation will have to be done. All the work reported in this paper deals with annealed brasses. What Mr. Crampton has done deals with cold-worked brasses. As will appear in my discussion of Mr. Crampton's paper, there are other factors which have a possible effect, and I cannot predict whether the effect that I have reported, which after all is a small one, would carry over and be felt in the cold-worked brasses.

Reclaiming Non-ferrous Scrap Metals at Manufacturing Plants

By Francis N. Flynn,* Milwaukee, Wis.

MANY excellent papers, descriptive of the milling and smelting of every kind of commercial ores, the refining of virgin metals, the casting into various shapes demanded by the trade, the rolling into shapes best suited to the factory machinery and the making of composition alloys to suit every requirement have been issued by the many technical societies dealing with non-ferrous metals. It is a wonderful collection of papers, of which the mining and metallurgical engineers may well be proud, but strange as it may seem, metallurgists in general appear to take the stand that when they have delivered suitable alloys to the foundry and rolled products to the factory their duty to write papers has ceased, at least in so far as the A. I. M. E. is concerned. Still we read in the daily papers·that the mining companies are absorbing metal-manufacturing industries. The purpose of this paper is to describe the reclaiming of non-ferrous scrap metals at manufacturing plants, taking as an example the automobile industry.

COLLECTION AND DISPOSITION OF SCRAP

Until about five years ago, much of the factory scrap, with little or no preliminary treatment, was sold to secondary-metal smelters. Of late years the factory salvage department has become an important part of the plant in reclaiming everything of value and incidentally does much of the work formerly done by the smelters. Like most good things, it is sometimes overdone, and much work is done at the factory with inexperienced men that could be done much better by experienced skilled labor at the custom smelting plants.

Employees of the salvage department collect the waste products in all departments at the source and in that way avoid much contamination. Every reasonable precaution is taken to keep the scrap clean. It is hand-sorted, cut, burned, magnetized, concentrated, separated or compressed, as the case may be, preparatory for re-use in the plant or for selling to others.

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* Metallurgist.

Copper, tin, lead, zinc, aluminum, antimony and nickel are the principal metals in automobile manufacturing. Large tonnages of copper and tin are used in the bronze foundry, copper and aluminum in the aluminum bronze foundry, yellow brass strip and solder in the radiator department, tin in the babbitt department, antimony and lead in the battery department, and copper wire for electrical parts.

The manufacturers' aim is to re-use the clean scrap by the simple process of melting rather than smelting. Most of this work is carried out in the foundries on the night shift to avoid interference with production work on the day shift. The kettles or furnaces that are used for making production castings are used for melting the reclaimed scrap metals. The capacity of the kettles varies from 1 to 20 tons, whereas that of the melting furnaces varies from ½ to 1 ton. The melted scrap is poured into pig molds for re-use when and as required.

Not all of the scrap is melted; much is sold as collected, because there is no use for it in the foundries. There is a surplus of wrought yellow brass clips and borings, which if clean, bring a high price in the market. Chunk brass is not melted to pig but, because of the quantity used, it is advisable to melt and pig all borings of a copper-base alloy. The classification of scrap, the method of reclaiming and its final disposition is summarized in Table 1.

TABLE 1.—*Classification, Reclamation and Final Disposition of Scrap*

1. Sold to brass rolling mills:
    a. Yellow brass borings: Cu, 62; Zn, 36; Pb, 2.
    b. Yellow brass clips: Cu, 65; Zn, 35.
    c. Yellow brass punchings: Cu, 65; Zn, 35.
2. Utilized:
    a. Small yellow brass punchings: Cu, 65; Zn, 35.
       A portion is melted with virgin zinc and granulated in water to small shot size. Equal quantities of punchings and shot are mixed with borax and used as brazing compound.
3. Substituted for virgin metal in the brass foundry:
    a. Copper clips and slugs.
    b. Copper punchings.
    c. Copper wire shellac coated.
    d. Copper wire solder coated.
    e. Copper forgings.
    f. Brass forgings.
4. Substituted for virgin aluminum in the aluminum die-cast foundry:
    a. Wrought aluminum.
5. Substituted for virgin metals in the aluminum bronze foundry:
    a. Aluminum bronze forgings.
6. Melted to pig in aluminum bronze melting furnace:
    a. Aluminum bronze chips and borings: Cu, 90; Al, 10.
7. Melted to pig in brass foundry melting furnaces:
    a. Insulated wire, burned and compressed: Cu, 97; Sn, 1.25; Pb, 1.25.
    b. Wrought copper borings: Cu, 95.

     c. Soldered copper shapes: Cu, 92; Sn, 4; Pb, 4.
     d. Radiator fins and tubes: Cu, 73; Sn, 4; Pb, 4; Zn, 19.
     e. Radiators: Cu, 78; Sn, 3.5; Pb, 3.5; Zn, 15.
     f. Phosphor bronze borings: Cu, 89; Sn, 11.
     g. Phosphor bronze borings: Cu, 80; Sn, 10; Pb, 10.
     h. Red brass borings: Cu, 87; Sn, 8; Pb, 2; Zn, 3.
     i. Yellow brass borings: Cu, 79; Sn, 2; Pb, 3; Zn, 16.
     j. Bearing borings: Cu, 88; Sn, 6; Pb, 6.
     k. Bearing borings: Cu, 85; Sn, 8; Pb, 4; Zn, 3.
     l. Bearing borings: Cu, 84; Sn, 6; Pb, 10.
     m. Bearing borings: Cu, 83; Sn, 11; Pb, 6.
     n. Journal backs: Cu, 79; Sn, 8; Pb, 13.
     o. Lead bronze borings: Cu, 70; Sn, 5; Pb, 25.

8. Melted in aluminum die-cast foundry kettles with virgin aluminum for direct castings:
     a. Crankcase borings: Cu, 8; Zn, 2; Al, 88.
     b. Piston borings: Cu, 10; Al, 87.5; Mg., 0.15.
     c. Foundry flasks: Cu, 8; Al, 91.
     d. "Y" metal borings: Cu, 4; Ni, 2; Al, 92; Mg, 1.5.

9. Melted in zinc die-cast foundry kettles with virgin metals for direct casting:
     a. Zinc borings: Cu, 3; Al, 4; Zn, 93.

10. Subjected to wet grinding, screening and gravity concentration on tables; concentrate dried and passed over a magnet machine:
     a. Factory floor sweepings.
     b. Aluminum bronze foundry cleanings.
     c. Brass foundry cleanings.

11. Sold to custom smelters:
     a. Concentrates (from 10).
     b. Mixed borings.
     c. Miscellaneous wrought scrap with iron.
     d. Grindings and buffings.
     e. Nickel alloys.
     f. Plating anodes.
     g. Electric lamps, fuses, coils and dry batteries.
     h. Aluminum die-cast skimmings.
     i. Zinc die-cast skimmings.
     j. Lead dross.
     k. Insulated copper cable.
     l. Solder dross.
     m. High-lead babbitt dross.
     n. Low-lead babbitt dross.
     o. Mixed bronze and babbitt borings and broachings. This product is screened, the ⅛-in. oversize is melted in kettles and the resulting dross is sold. The ⅛-in. undersize is difficult to melt without overheating and alloying the bronze and babbitt, therefore it is sold without being treated.

12. Scrap babbitt. Reduced in shallow brick shaft furnaces by gas and scrap wood to pig metal, which is remelted in kettles and used as machinery babbitt.

13. Scrap solder: Reduced in the same manner as babbitt, except that the copper is removed while in the kettle by stirring in sulfur. The copper-free solder is pumped into water-jacketed cylindrical molds for extruding. Solder floor sweepings are "sweated" in a small reverberatory furnace.

14. Scrap antimonial lead: Attempts have been made to reduce scrap batteries with gas and charcoal in shaft furnaces, lined with magnesite brick, with nichrome

grates. One-half to two-thirds of the metal was recovered while the residue had to be smelted. The cost of the combined processes was greater than direct smelting and the process was abandoned. The resulting antimonal lead was treated with sulfur to remove the copper before casting into ingot molds.

15. Cupola smelting. See special description.

CUPOLA SMELTING

The larger foundries find it more convenient to smelt a portion of their scrap than to sell it. This applies mainly to the concentrate and metal from the foundry cleanings and ladle shells and to a portion of group 11. A pig-iron melting cupola is used. After smelting for 8 hr. the bottom is dropped, the fireclay blocks are repaired and the furnace made ready for smelting another class of metal on the following morning. One furnace is used exclusively for lead. The charge consists of reclaimed metal from various alloys, usually a different alloy each day (Table 2).

TABLE 2.—*Charge in Cupola Smelting of Scrap*

Alloy	Coke, Pounds	Limerock, Pounds	Fluorspar, Pounds	Iron Scale, Pounds	Reclaimed Metal, Pounds
Antimonial lead.........	100	50	25	55	800
Aluminum bronze........	100	75	75	None	825
Yellow brass............	100	70	25	5	1000
Red brass..............	100	70	25	5	1000

The slags produced are remarkably clean in metal in chemically combined state; such loss as occurs is in metal prills. The analysis shows:

	SiO_2, Per Cent.	Al_2O_3, Per Cent.	FeO, Per Cent.	CaO, Per Cent.	MgO, Per Cent.
Low.....................	20	11	Trace	26	2
High....................	38	50	9	35	4

The lead slags show about 11 per cent. alumina and 9 per cent. iron oxide. The aluminum bronze charge contains slag resulting from the firebrick lining of the aluminum bronze melting furnace, together with oxidized metal from those furnaces. When smelted in a brick-lined cupola, the cupola slag shows up to 50 per cent. alumina. Whatever iron is present is carried into the metal by the aluminum. This charge could not be smelted by itself in a water-jacketed cupola because of the high alumina and the absence of iron. The red and yellow brass slags show less than 5 per cent. iron oxide.

The brick-lined cupola demands a slag low in iron oxide and high in lime with part of the limerock replaced by fluorspar. The metal produced analyses as shown in Table 3.

TABLE 3.—*Metal Produced in Brick-lined Cupola*

Metal	Cu, Per Cent.	Sn, Per Cent.	Pb, Per Cent.	Zn, Per Cent.	Sb, Per Cent.	Fe, Per Cent.	Si, Per Cent.	Al, Per Cent.
Antimonial lead..	0.1		95.5		4.4			
Aluminum bronze	96.0					1.5	1.5	0.75
Yellow brass.....	89.0	1.5	2 5	7.0		0.05		
Red brass.......	88.5	6.5	1.75	3.0		0.05		

The red and yellow brass metal contains less than 0.10 per cent. iron. When used with virgin metal it makes good castings. If the same charges were smelted in a water-jacketed cupola with the necessary iron flux added, the resulting metal would contain too much iron to be used for castings, without first having been refined in a reverberatory furnace.

As a result of smelting 8 hr. per day, there is produced from 10 to 12 tons of metal per furnace.

The advantages gained by smelting in a brick-lined cupola over a water-jacketed cupola are:

1. Many hours saved in warming up the furnace preparatory to smelting.

2. The brass-foundry workmen are more familiar with the operation of a pig-iron melting furnace than with a water-jacketed cupola.

3. Slags can be made practically free from iron and high in alumina.

4. Metal can be made lower in iron, a most important consideration.

5. A furnace campaign lasts one shift instead of a week or more.

The only disadvantage is the patching of the firebrick lining after each run. Two men can patch a furnace and charge the kindling and coke bed on one shift in exactly the same manner as in iron melting.

The brick-lined iron-melting cupola when used for smelting non-ferrous metals should differ from one used for iron; the distance between tuyeres and the bottom should be from 6 to 12 in. greater. This greater depth is recommended to provide for a thicker sand bottom and a larger volume of metal and slag at low temperatures. The furnace is operated in the same manner as a water-jacketed black copper furnace but because of the brick lining it is necessary to run on a low volume of air.

DISCUSSION

E. R. DARBY, Detroit, Mich.—There is nothing new in the statement that the author sells a mixed bronze and babbitt turning to the smelter. It seems there ought to be some wise person who can devise a means of separating economically the babbitt chips from the bronze which are contaminated during the turning operation. It is

important and would be of inestimable value to plants manufacturing the babbitt line bronze-back bearings.

The author enters into the subject of smelting of bronze foundry waste and battery lead waste in a brick-lined cupola. This is somewhat different from the practice of some concerns. The use of water-jacketed blast furnaces is prevalent, and the use of brick-lined cupolas is interesting. He shows that some of his slags run as hig has 50 per cent. in Al_2O_3. This is very high, and makes the slag rather hard to handle. He uses a considerable amount of fluorspar, and it is interesting to note that the purity of the metal coming from such a smelting operation is much higher than that from the smelting operation where iron oxide or some form of material containing iron oxide is used as a flux.

A. T. MARCH, Chicago, Ill. (written discussion).—I believe that the author covers the general principles of non-ferrous scrap reclamation. At the Hawthorne plant of the Western Electric Co., when possible we segregate non-ferrous process scrap at its source, as this ensures a better product. As a precautionary measure against contamination by foreign material, the scrap is inspected after receipt by the By-Products Department. Miscellaneous scrap is classified by experienced sorters, some of whom have had many years' training in this line and have become experts on this work. Inexperienced labor is not used for sorting.

Our engineers are constantly at work to improve methods of segregation and classification in order that a higher grade by-product may result.

The conversion of secondary copper into wire bars as described by Messrs. Scheuch and Scott[1] is the outgrowth of these efforts, as is also the re-use of reclaimed lead sheath in the manufacture of lead cable sheath. Only recently improvements in the sorting of junk lead sheath have been developed which have added materially to the tonnage of reclaimed lead that can be re-used economically in the manufacture of lead-covered cable.

H. J. BEATTIE, Schenectady, N. Y.—It is gratifying to those of us who are devoting a good share of our time to salvage work to see a society like the American Institute of Mining and Metallurgical Engineers take the initiative in the interest of secondary metals.

The various plants of the General Electric Co. are well organized to collect and dispose of waste products. The classification of the non-ferrous metal is similar to that given by Mr. Flynn; it consists of 22 classes which are subdivided into about 125 classes, each having a separate market price.

A few figures will serve to show the importance of the non-ferrous metal in our salvage departments from a dollars and cents standpoint. About 88 per cent. of the tonnage of metal scrap consists of iron and steel, with an average scrap value of $9 per ton, which represents only 25 per cent. of the total sales value. The remaining 12 per cent. consists of non-ferrous scrap, with an average scrap value of $183 per ton, or 75 per cent. of the total sales value. It follows naturally therefore that the main work of our salvage department is in collecting, classifying and disposing of non-ferrous scrap.

We accumulate more scrap metals than can be used in our foundries. The tendency, therefore, has been to take the cream of the accumulation, which is the good copper and has a sales value nearest to the virgin metal.

Within the last two years new melting furnaces have been installed in the foundries, so that now we utilize alloy scrap such as turnings, castings, etc., which heretofore were sold on the outside at a sacrifice of at least 4c. per pound. By taking precautions

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[1] See page 289.

to keep the scrap clean and segregated, it is possible to melt for direct casting and eliminate the intermediate step of pigging.

D. L. COLWELL, Chicago, Ill.—I should like to utter a warning in regard to the practice the author gives in item 9 of Table 1. He says, "Melted in zinc die-cast foundry kettles with virgin metals for direct casting: a. Zinc Borings: Cu, 3; Al, 4; Zn, 93."

That particular alloy is very susceptible to aging, that is, embrittlement and growth with age, if certain impurities are allowed to get too high, notably tin, lead and cadmium. In a plant where the amount of tin, lead and bronze is melted that is indicated here, it would be exceedingly dangerous to use those borings in die castings again. The castings made of that material would not be representative of the best die-casting practice.

It is a fact that many such die castings find their way to the market, and they are doing harm to the reputation of die casting. If we could be absolutely sure that all of the zinc-base die castings on the market were what they should be with regard to impurities we would have little trouble in applying die castings to three or four times their present uses.

We think that where there is any possible danger of the contamination of die-casting borings with other metals, they should not be used in making die castings again.

R. W. DRIER, Houghton, Mich.—About a year ago we tried to work out a solution for the problem of separation of brass and babbitt. We tried it both by electrostatic means and by flotation, and although we did not get as far as we would like to with the problem, we did find that in the electrostatic process we could make a fairly clean babbitt separation, the concentrate being babbitt with a little brass. We hoped to get a machine that would handle a higher voltage than we were using, which was about 30,000 volts.

In the flotation work we were able to separate a very clean brass concentrate, but this was not satisfactory either, because the material we were using was composed of turnings and scrapings and filings combined. The corkscrew-shaped particles clung together, hindering separation, but we thought that if we could have a size and shape separation before we tried flotation we could separate the brass.

E. R. DARBY.—I am rather surprised that Mr. Flynn finds it necessary to melt into ingot borings from his own plant. With the history of the turnings well in hand, I should think it would be safe to put them directly into the casting, and certainly it would be much cheaper to do so.

In connection with the brick-lined cupola for smelting, it has been my experience that such a cupola is satisfactory provided it can be shut down at the end of a few hours. If the smelting material where the flux used has to be extremely basic, the lining will not last very long unless the cupola is shut down at rather short intervals and patched thoroughly. For continuous smelting, in which a furnace is run for weeks and months, sometimes years, I cannot believe that a brick-lined cupola can be used.

It has been the practice in plants with which I have been connected to save the waste until sufficient was on hand to warrant a rather extended run, and for this I believe that a water-jacketed furnace is better. Of course the metal from such a furnace is not as pure as that described by Mr. Flynn, and I am deeply interested in the purity that he describes. With a water-jacketed furnace making a slag that is perhaps 20 to 25 per cent. iron, and about 14 to 18 per cent. lime, with 34 to 37 per cent. silica, the iron content of the metal recovered will run perhaps as high as 1 per cent., which means that it must be refined afterwards. Even so, I believe that the refining operation connected with the water-jacketed furnace will be cheaper than the repair bills for the cupola.

F. N. FLYNN (written discussion).—Referring to Mr. Colwell's remarks: All metals used are virgin metals. The castings are machined in the melting room, where there are no other alloys present.

Mr. Drier's experiments with brass and babbitt mixtures are interesting. Assuming that the flotation process could be made a metallurgical success, it is questionable whether such an installation could secure a sufficient tonnage of fine borings to warrant using the process. The chemistry of the flotation reagents requires the continuous services of expert operators at salaries beyond the reach of small-tonnage plants. On the other hand, if the electrostatic process could be developed to a metallurgical success, it could be operated intermittently at a nominal cost by a man of average intelligence and training.

With reference to Mr. Darby's remarks on cupola smelting: The problem that confronts the brass foundryman is to reclaim in usable metal the following by-products:

1. Metal furnace slag and ladle skimmings.
2. Floor cleanings.
3. Concentrate.
4. Ladle skulls.
5. Mixed metals, usually borings, with aluminum or antimony.
6. Metal resulting from "bad heats" or "white heats," usually containing less than 0.05 per cent. silicon or aluminum, in red brass or tin bronze.

The melting-furnace slag, ladle skimmings and floor cleanings can be concentrated advantageously, and the resulting concentrate dried and fed back into the melting-furnace mixture.

The ladle skulls, mixed metals and bad heats usually can be returned to the melting-furnace mixture in small amounts to every charge, provided that mixture contains sufficient new ingot metal to dilute the impurities.

If the above procedure does not meet the situation, and it becomes advisable to install a cupola because of the larger tonnage, such a furnace operating one day a week should be sufficient to keep the by-products worked up. To meet this problem a brick-lined cupola is recommended for items 3, 4, 5 and 6. Melting-furnace slag cannot be economically smelted in a brick-lined furnace.

When metallic iron enters the brass cupola, all of it will be alloyed with the brass, regardless of the construction of the furnace walls. When iron oxide flux is added, a larger percentage of iron will be found in the resulting brass, because a small portion of it is reduced by the fuel, the amount bearing a direct relation to the fuel percentage. The metallic iron in brass cupola metal is always greater in a water-jacketed cupola than in one lined with brick, because of the increased amounts of iron oxide and coke used.

Not all the iron will leave the furnace with the brass; an iron alloyed with a little brass will remain in the furnace as a sow, gradually building up on the bottom and sides until it stops the furnace after one to three week's operation. It then requires one week to remove the sow and reline the bottom, unless the cupola happens to have a separate removable bottom, when one to two days will suffice.

Brass cupola metal as pigged is full of gas, contains a little sulfur, and the impurities vary considerably from hour to hour. It is unfit for making castings unless used in small quantities with reverberatory refined ingot.

The brick-lined cupola meets the brass foundryman's requirements much better than a water-jacketed cupola. The tonnage of scrap to be reclaimed is much too small to warrant even consideration of the reverberatory refining furnace.

Mr. Darby's comments regarding the pigging of bronze borings are quite in order. In the average foundry the borings are not pigged, but there are exceptional foundries where it becomes necessary to deviate from the standard practice to improve the physical condition of the metal mixture, in order to reduce the percentage of scrap.

For purposes of illustration only, two melting-furnace charges are compared in Table 4. It is understood, of course, that these arbitrary figures vary for different alloy mixtures.

TABLE 4.—*Comparison of Furnace Charges*

	Average Foundry, Per Cent.	Exceptional Foundry, Per Cent.
Gates..	20	15
Foundry and machine-shop scrap.........................	5	5
Borings...	20	
Pigged borings..		25
Purchased wrought scrap................................	15	5
Purchased cast scrap...................................	5	15
Reclaim concentrate....................................	5	
Reclaim blast-furnace pig..............................		15
Purchased composition ingot............................	30	
Purchased virgin-metal ingot...........................		20
	100	100
Impurities in purchased cast scrap or "chunk brass".......	Normal	High
Quality of blast-furnace metal..........................		Poor
Melting furnace atmosphere.............................	Oxidizing	Reducing
Carbon compounds in oils and machine-shop cutting solutions in wet borings.......................................	Low	High

If the borings are not pigged, the percentage of scrap castings produced will be increased slightly in tin bronze, considerably in red brass, doubled in yellow brass, and trebled in aluminum bronze.

When these wet borings are charged into the melting furnace, 500 lb. in a 2000-lb. mixture, it is necessary to hold the 1500-lb. remaining charge until the borings have been rocked for from 15 to 30 min. with the furnace door open, to burn off the carbon compounds. This necessary practice cools down the furnace, increasing the melting time, and interferes with metal production during the rush hours. When borings are pigged, the same furnaces are used on the night shift. The furnace is filled with borings, the furnace door put on and the current turned on, and as soon as the melt runs freely it is pigged.

A. H. HOBLEY, Washington, D. C.—I would like to explain the interest of the War Department in the utilization of secondary metals and the reclamation of scrap materials.

After the last war, Congress passed the National Defense Act, which requires the Assistant Secretary of War to make a study of certain problems that occurred during the war, and to determine the measures necessary to prevent a recurrence of some of these problems in event of another emergency. In performing this work, the War Department has established an organization which supervises the work of the Supply Services in determining their needs in various materials, and which makes a study of the possible resources of the country to meet these needs and the extent to which industry would thereby be affected.

As you know, the consumption of certain metals increases rapidly in time of war—for instance, copper. In this particular case it happens that our domestic resources eliminate any great cause for concern, because we believe that we can get all of the

copper we may need, but there are other metals that are not available in this country in sufficient quantity to meet anticipated needs. We refer to these metals as "strategic materials."

The conservation of domestic resources is one thing, but the conservation of resources which we do not possess at all or in very limited quantities is another—for instance, chromium. Until about 1850, this country was the world's principal source of supply of the mineral chromite, which is the source of chromium. At that time, however, richer foreign resources were discovered, which affected our chromite industry to such an extent that at the outbreak of the war this country was importing practically its entire consumption. The possession of domestic chromite deposits, however, enabled the country to produce a large quantity of chromium during the war and thus avoid the possibility of a serious shortage.

There are other metals, such as antimony and tin, in which we are not so fortunately favored and it is in these that economic wisdom dictates the importance of utilizing secondary sources of supply or scrap material, in peace time, in order to develop the methods and necessary system that would be available for use in an emergency. If these methods have been developed so that it is possible to reclaim those metals of which there might be a scarcity, the domestic industry will be in a much better position than if it has to depend upon using such supplies as are available after the military demands have been provided. Incidentally, of course, reclaimed or scrap metal should also be used in meeting military demands as far as they are suitable for the purpose.

In war time entirely new uses arise for old materials. Consider antimony, for instance. In peace time 75 per cent. of the consumption is taken by type metal, antifriction bearings for machinery, Britannia metal and antimonial lead. The military uses, which would arise in war time, are as antimonial lead for shrapnel balls, in primers, and to produce a white smoke for range-finding. Any means by which the peace-time uses could be provided for would thus make available a supply for the additional military requirements in war time and to this extent obviate the necessity for using a substitute for either the commercial or military uses. Some consideration has been given to the use of a substitute for antimony in the military requirements, and it has been determined that Frary metal, for instance, and other substances such as calcium and barium, can be used in certain cases. These are all more expensive than antimony, however, and the development of a means for reclaiming antimony in order to reduce the requirements for virgin metal would thus make unnecessary the use of a more expensive substitute, or at least reduce the quantity that would be required.

T. A. WRIGHT, New York N. Y.—Judging from what I see of the reclaiming of metals today, and the particular progress that is going on in certain of the refineries, particularly in reference to tin, I think we are going to emulate the stockyards. Solder of exceptionally high purity is produced today from radiators, in carload lots. Tin is reclaimed today from material which formerly went into the blast-furnace slags. Germany, several years ago, was taking large quantities of zinc and of tin that we could not reclaim here. Even zinc oxide of a fair purity is reclaimed today from refining operation of scrap, which the foundry, in the first place, and the smelter, in the second place, cannot use.

I believe we are fully alert to the importance of that, not only in the tonnage, but in the monetary value. The tonnage has increased since the war figures mentioned by Mr. Dunlop in his paper of two years ago[2] but I notice that the total values have not particularly increased.

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[2] J. P. Dunlop: Non-ferrous Secondary Metals Recovered in the United States. *Proc.* Inst. Metals Div., A. I. M. E. (1928) 660.

Recovery of Waste from Tin-base Babbitting Operation

By P. J. Potter,* Detroit, Mich.

Practically all tin-base babbitt metals used in engine bearings are made to customers' specifications, which are many and varied. The copper ranges from 3 to 8 per cent. and the antimony from 4 to 13 per cent.; generally, the babbitt with lower copper content will contain from 4 to 8 per cent. antimony and that with higher copper will have from 7 to 13 per cent. antimony. The allowable lead content varies from 0.20 to 2.00 per cent. If a solder is used as a bonding material instead of tin, the resulting material in the finished bearing will have a higher lead content, but it would not be enough to bring the lead above specificational limits. Impurities such as iron, arsenic and bismuth should be determined in the tin before using to insure a uniform and high-grade product. These points must be considered when segregating and grading the waste that comes from the finishing operations on lined bearings.

Classification of Scrap

Because of the extremely rigid nature of most of the specifications for bearing linings it is necessary to use the purest of materials as a base for all compositions. The problem of handling secondary metals is confined almost entirely to the recovery of drosses, spills and turnings incident to the manufacturing operations. As a matter of convenience the waste or scrap may be divided into 10 grades, as follows:

1. Tin from pots where tinning operation is carried out.
2. Tin and babbitt spatters from babbitting operation.
3. Tin skimmings combined with burned zinc chloride.
4. Borings and reamings.
5. Gates from die-cast bushings and bearings.
6 Drosses from die-cast pots, babbitt foundry pots, and pots in babbitting room.
7. Babbitt with small amount of bronze from machining operations.
8. Babbitt and bronze borings.
9. Scrap bronze-back babbitt-lined bearings.
10. Scrap die-cast bearings and bushings.

A few of these grades of salvaged material have compositions that make it possible to determine beforehand where they may be used to

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greatest advantage; a few may be used after a simple melting followed by analysis, while others require sweating or smelting followed by an extra cleaning operation to bring the finished ingot to the necessary high degree of purity.

METHODS OF HANDLING SCRAP LISTED

1. Since the tin used in the tinning operation dissolves an appreciable amount of copper and zinc from the bearings being tinned, it becomes necessary to remove the impure tin periodically and replace it by pure metal. The metal removed from the pots is agitated with steam for the purpose of drossing off the zinc, and the remaining clean tin-copper alloy is used in babbitt mixtures where specificational limits permit of its incorporation. The drosses from this purification are smelted as in grade 6.

2. In connection with tinning and babbitting operations there are always some spatters and spills of high metallic content. This class of material is swept from around the tin and babbitt kettles and is sweated in an oil-fired reverberatory furnace at a moderately low temperature. The resulting metal is collected in a receiving pot and the traces of zinc are removed as in grade 1. It is then ready for use in babbitt mixtures. The residue from the sweating operation is in the form of dross and is reduced to metal by the smelting process, as described later.

3. The skimmings from the kettles are always contaminated with fused tinning flux; they are sweated in a reverberatory furnace and the resulting metal and dross are treated as above.

4. The turnings, punchings and broachings that are absolutely clean, free from iron, steel, bronze or other contaminations, are returned to the babbitt department and melted in a large kettle. The melt is freed from oxides, iron and non-metallic inclusions by treating with sulfur and rosin and the accompanying drosses are reserved for smelting. The cleaned melt is immediately analyzed and 50 per cent. or more new metal is added in the correct proportions to bring the whole quantity to the desired specification.

It is usually unnecessary to classify the turnings and chips before treating as described, as the heavy dilution with 50 per cent. or more new metal will take care of specificational requirements in nearly all instances.

5. Gates and scrap from the die-casting operations are returned to the babbitt department and treated exactly as turnings and chips from lined bearings.

6. Drosses from all kettles and from the sweating furnace are mixed with coal or any other good reducing agent and reduced to metal in a smelting reverberatory. The metal from this furnace is tapped into

a large receiving kettle and is refined with steam sulfur and rosin according to the nature of the individual charge. The slags formed during smelting are usually low in metal and are discarded. They are, however, carefully assayed and when necessary are returned to the furnace for additional reduction.

7. In some finishing operations it is impossible to remove babbitt without cutting some bronze. Such material is sweated at a low temperature, so as to keep as much bronze as possible in the residue. The resulting babbitt will be rather high in copper and will contain some zinc and lead. The zinc is removed by refining as in paragraph 1 and the lead is reduced by dilution. The residue from the sweating operation is absorbed by the bronze foundry and the drosses from refining are added to other drosses for smelting.

8. From various finishing operations there will always accumulate some mixed bronze and babbitt chips and turnings. As the babbitt particles are in the main larger than the bronze, a separation by double screening is fairly effective. The coarse screen, 6 mesh, removes the heavy babbitt, which is added to class 7. The second screen used is 12 mesh, and the particles held upon it are sweated separately. The resulting metal, after refining for removal of zinc, must be strongly diluted with new metal, as its copper content is high. The remainder of this class and of that which passes the second screen is absorbed by the bronze foundry or sold as occasion or market may determine.

9. Scrap bronze-back babbitt-lined bearings are sweated to remove the babbitt. The babbitt obtained is refined and cleaned, then pigged and used where specification permits. The residue bronze is returned to the bronze foundry.

10. See Paragraph 5.

Manufacture of Wire Bars from Secondary Copper

By W. A. Scheuch* and J. Walter Scott,* Chicago, Ill.

Ordinarily secondary copper, unless electrolytically refined, is reclaimed directly as foundry ingots used in the manufacture of copper-rich alloy castings. This use does not require the elimination of the impurities to the degree required if the recovered metal is to be used for electrical purposes where a high electrical conductivity is of prime importance.

However, as a part of the general policy of reusing its own scrap and by-products wherever possible, the Western Electric Co. at its Hawthorne Works is recovering its secondary copper as wire bars which are delivered to its own rod and wire mill and there processed into wire of high electrical conductivity. This departure from the usual recovery scheme has been accomplished through the careful classification and sorting of the material entering the furnace charges and the careful control of the subsequent melting and refining in a reverberatory furnace. Tests conducted over a period of approximately four years have shown that the quality of wire bars produced from selected secondary copper is equal to that of wire bars produced by the electrolytic refineries.

The interest which has been exhibited in the process by those who have seen it has prompted the following general description. It is the authors' opinion that the recovery of secondary copper will become more and more an important factor in the copper production industry.

The description is largely of the refining furnace and its operation, but it must be remembered that careful classification and sorting of the scrap materials to eliminate impurities are just as important as the furnace operation toward obtaining a satisfactory final product. Classification and sorting do not lend themselves easily to description; they must just be done. It should also be recognized at the outset that constant intelligent supervision is requisite to the success of the process because there are so many ways in which impurities can find their way into the final product.

Secondary Copper Used for Wire Bars

Only clean secondary copper of the grades known to the trade as Numbers 1 and 2 are melted for wire-bar manufacture. This material, supplemented by that obtained from various manufacturing processes

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within the Western Electric Co., consists primarily of copper wire purchased as obsolete equipment from the various telephone companies. Specifically, the secondary copper consists almost entirely of the following items:

1. *Old Line Wire.*—This classification covers telephone and telegraph wires torn down in the field and purchased by the Western Electric Co. It is usually obtained as well-formed coils varying in weight from a few pounds to 600 lb., although in some cases, because of storms in the field, the wire may be tangled and hard to handle. The fact that this material is sometimes shipped in cars also containing lead-covered cable means that care must be taken to keep out lead as an impurity. The wire is usually coated with weathering products, a particular one of which occurs on wire coming from localities near the oceans, and probably consists largely of copper chloride. When heated, this coated wire fumes badly and causes discomfort to the operators unless they wear respirators.

2. *Rod-mill Scrap.*—This consists of ends and rejected copper rods from the hot rod-rolling mill. Material is either cut into short lengths, heavy slabs, or wound into bundles weighing approximately 100 lb. each. The copper is coated with oxide and contains some grease.

3. *Wire-mill Scrap.*—This consists of copper wire scrap from the wire-drawing process. In general the wire is made into bundles or bales weighing approximately 100 lb. each. A small amount of scrap is delivered to the furnace as loose wire or in coils from 6 to 18 in. dia., weighing only a few pounds.

4. *Copper Oxide Scale.*—This is the scale that flakes off the copper bar and rod during the hot rolling process. It contains approximately 5 per cent. moisture and approximately 85 per cent. copper (dry basis). The impurities are tramp iron and grease from the rolls.

Furnace Charge

A typical furnace charge consists of material mixed in the following approximate quantities: line wire, 50,000 lb.; rod-mill scrap, 10,000 lb.; wire-mill scrap, 25,000 lb.; copper oxide scale, 5000 lb. It is not implied, however, that it is necessary to use these proportions or even to mix the classes of materials, a charge consisting entirely of any one kind of scrap other than the scale will produce satisfactory wire bars.

LAYOUT OF REFINERY

Fig. 1 shows the refinery layout plan. The furnace and auxiliary casting equipment are housed in a building 50 by 70 ft. The furnace occupies a space approximately 15 by 25 ft. at one end of the building while the casting area extends from the front of the furnace to the other end of the building. There are eight horizontal mold positions for

casting, four end to end on each of the two cooling water tanks. Experience has shown that it would be better to have 10 mold positions—five
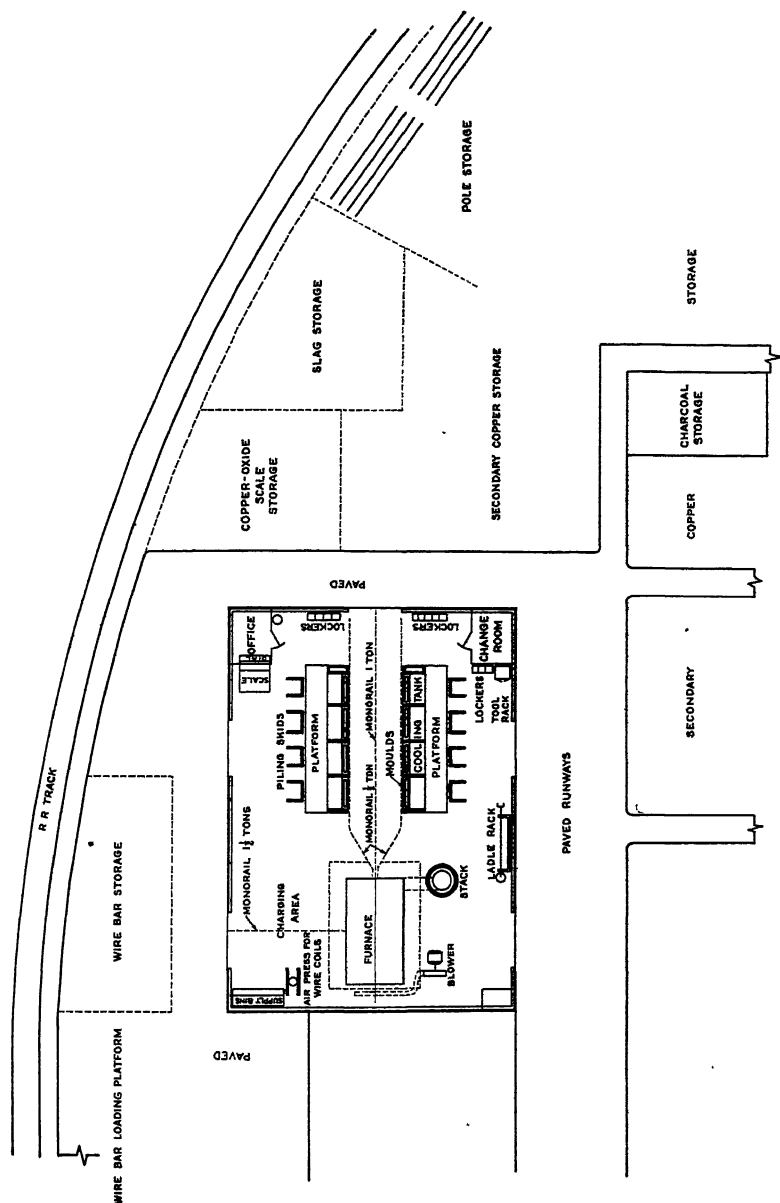
FIG. 1.—DIAGRAM OF GENERAL PLANT LAYOUT.

on each cooling water tank. The tanks are spaced approximately 10 ft. apart to give a working area between them. There is a clearance of 10 ft. between the front of the furnace and the first mold position; this

is provided in order to establish an easy radius on which to swing the trolley supporting the pouring ladle en route to the molds. Directly out of the center of the front door, extending over the area between the cooling tanks, is a trolley and chain-block for serving that area. The charging area is adjacent to the furnace side door and is served by still another trolley on which the charging paddle is supported. The furnace stack is approximately 10 ft. from the front corner of the furnace, and the blower, which is capable of furnishing 750 cu. ft. of air per minute at 2 lb. pressure to the two oil burners on the furnace, is similarly located near the rear corner. In one corner of the building is a small office and in another is a similar enclosure serving as a change room for the furnace operators.

The furnace building is surrounded on three sides by concrete runways which serve the storage yard. This yard has a total area of approxi-
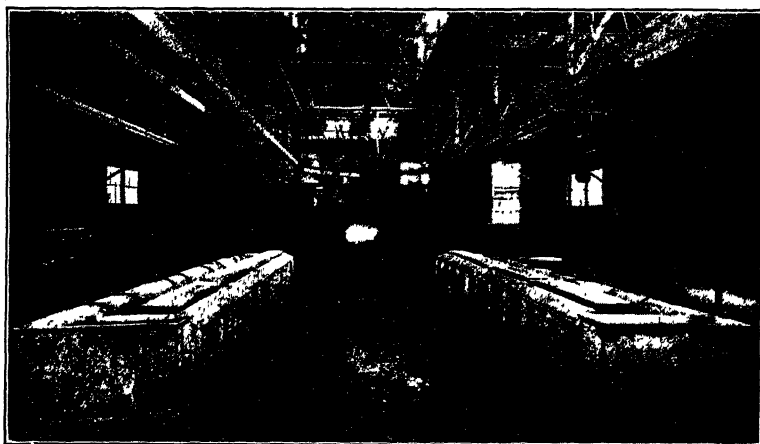
FIG. 2.—INTERIOR OF FURNACE BUILDING.

mately 15,000 sq. ft. and the 6000 sq. ft. devoted to copper storage will accommodate a reserve supply of approximately 1,500,000 lb. of scrap copper wire. Practically all the copper scrap is supplied to the refinery on skids and as many loaded skids as possible are allowed to remain on the runways, thus avoiding the unloading and reloading of that particular material. Since the runways will accommodate more than three days' supply of scrap on skids, and since there is a rather uniform flow of material to the department, the ground storage is used primarily as reserve. The copper oxide scale storage and the slag storage are adjacent to the railroad tracks, so these materials may be conveniently handled with a locomotive crane.

A charcoal bin that will hold two carloads of charcoal and a pole-storage yard that will accommodate approximately six carloads of poles are near the tracks in convenient positions for unloading.

Storage space for approximately 200,000 lb. of wire bars is available on the concrete walk close to the railroad siding, where the wire bars may be conveniently loaded into box cars and switched to the rod mill. After the wire bars have been removed from the cooling water tanks singly they are handled entirely in bundles of 24. The bars are stacked six wide by four high and are wired tightly together with two wires, so that they are readily handled by a special electric truck equipped with elevating tines to support the load.

FURNACE CONSTRUCTION

The furnace construction follows more or less closely the general construction of copper-refining reverberatory furnaces. It has inside hearth dimensions of 13 ft. 0 in. long by 7 ft. 3 in. wide, tapering to 4 ft. 6 in. wide at the front, and provides for a metal depth of 2 ft. 0 in. at the front decreasing to approximately 1 ft. 3 in. at the back, or an average metal depth of 1 ft. 9 in. throughout. These dimensions allow a maximum capacity of 90,000 lb. without overloading.

The foundation and furnace pit are made of reenforced concrete, on which are built brick piers to support the furnace and provide ventilation under the furnace bottom.

The bottom plates of cast iron 2 in. thick rest on the brick piers and the side and end plates of steel $1\frac{1}{2}$ in. thick run from the bottom plate to the height of the metal line, thus enclosing the lower part of the furnace.

The refractory bottom is built on the cast-iron plates. It consists of a 12-in. silica brick inverted arch superimposed on a firebrick arch.[1] These arches are built on an inside radius of 11 ft. 0 in. The curved bottom for the arches is built up of firebrick on the bottom plates. The bottom extends from side plate to side plate and it is flattened off at the sides to support the side walls. The joint made by the bottom and side walls is sanded to insure metal-tight construction.

The side walls are vertical up to a point two courses above the metal line and consist of 9-in. magnesite brick backed up by 9 in. of firebrick. The three courses at the metal line are magnesite straight through to the outside of the wall. It is believed that the heat is conducted through the wall a little more rapidly, thus keeping the metal line a little cooler and reducing the rate of corrosion, which is greatest at this point. Above the metal line, the inside of the wall is stepped back about $\frac{3}{4}$ in. at each course. This tends to delay the falling in of the wall when the brick work has corroded away at the metal line. It starts with 9 in. of magnesite and 9 in. of firebrick bonded together so that the minimum thickness of magnesite is 9 in. Where the side walls join the roof arch the walls

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[1] It is now believed that it would have been better construction to have built two superimposed inverted arches each of 12-in. silica brick.

have been stepped back to such an extent that the thickness is 9 in., consisting of 4½ in. of magnesite backed by 4½ in. of firebrick.

At points approximately 4 ft. 0 in. from the front breast, the side walls taper from 7 ft. 3 in. wide across the center of the front to 4 ft. 6 in. at the front breast. This taper furnishes a ledge against which it is possible to support a brand that is used to hold back the charcoal on the metal bath, so that the metal may be dipped from a clean surface. As an experiment, this taper was removed and the corners made square. There was no objection to this construction, except that the brand could not be held in place satisfactorily. The construction was therefore discarded in favor of the taper.

The two burner ports are 2 ft. 3 in. deep, 1 ft. 9 in. wide and 1 ft. 5 in. high at the large end. They are completely lined with 4½ in. of carborundum brick. The top of the port is a bonded arch made of 9-in. arch brick on a radius of 10½ in. The sloping bottoms of the burner ports are made of 9-in. key brick laid flat on a 2-ft. 6-in. radius with skewbacks in the side walls of the ports to prevent the key brick from sliding into the furnace.

The roof consists of a 12-in. silica brick arch on a radius of 11 ft. 0 in. This arch is not bonded, each ring extending separately across the furnace. This construction facilitates quick repairing of the arch in an emergency. The skewbacks at the ends of the arch rings are supported by a 12-in. channel on each side, which is riveted to the buckstays at the proper height. The distance to the center of the flat back section of roof arch from the metal surface is approximately 3 feet 0 inches.

The buckstays are made of 8-in. I-beams placed on approximately 2-ft. 0-in. centers except where doors, etc., make special construction necessary. Headers, consisting of two 4-in. channels, support the buckstays at top and bottom. These headers are connected together across the furnace at both top and bottom by 1¼-in steel tie rods. The ends of each rod are held against the headers by heavy steel springs.

Two oil burners supply the heat. They are placed in the back wall about 1 ft. 9.in. above the metal line and pointed down at an angle about 7° from the horizontal, so that the flames impinge on the metal surface at points opposite the charging door.

The charging (side) door is 4 ft. 0 in. wide and 2 ft. 0 in. high. The bottom of the door is an inverted magnesite arch which prevents the side wall beneath the door from breaking loose and floating up. The door jambs are of magnesite brick and the arch over the door is of carborundum.

The dipping (front) door is 3 ft. 0 in. wide by 1 ft. 4 in. high. The dipping-door sill is about 1 in. lower than the charging-door sill and is 2 ft. 2½ in. from the casting-area floor. In constructing a furnace for hand-dipping, one of the critical dimensions is the height of the dipping-

door sill as compared to the height of the molds, because the ladle must clear the door sill and yet be at proper height for pouring the metal into the molds. The dipping door is used for both poling and skimming, the poling and skimming supports being fastened to the buckstays at the sides of the door.

The flue is at the end of the furnace farthest from the burners and directly above the poling door. The height of the roof arch decreases at this end until, just at the flue, the "reverberatory" arch is only 14 in. above the metal line. The "reverberatory" arch is made of carborundum bricks on a radius of 11 ft. 0 in. This radius is considered to have the minimum spring and a smaller radius with skewbacks bedded into the sidewalls is a recommended construction. Another arch of silica is superimposed above this to take the weight of the brickwork above. As the expansion of the silica arch is much greater than that of the carborundum, care must be taken to put paper fillers, which will burn out, between the bricks, so that the expansion of the upper arch will not spread the furnace and allow the carborundum arch to fall. The use of silica in this arch is not entirely satisfactory. Firebrick has been tried and found unsatisfactory also. At present magnesite is being used as an experiment.

The waste gases are carried by a crossover from the furnace to the refractory-lined steel stack. The crossover is 1 ft. 4 in. by 2 ft. 7½ in. inside. It is made of 9-in. firebrick and is supported by a steel framework, tied in to the top of the buckstays to relieve the furnace arch of all weight. The stack is made of $\frac{5}{16}$-in. steel plates with 9-in. firebrick lining. The inside diameter of the lining is 3 ft. 6 in. The stack is 60 ft. high and the lining runs up about 30 feet.

The life of such a furnace lining averages between three and four months. Failure usually occurs from the heavy corrosion of the side walls at the metal line. Hot-patching the metal line has been tried but has not been entirely satisfactory. A complete relining repair requires a loss in operation of from 10 to 14 days. Every 6 to 8 weeks it is also necessary to replace the roof arches. This repair can be made in less than one day, but two days' operations are usually lost because of bringing the furnace back up to temperature. Minor repairs, such as patching the roof arches, door jambs, front breast, etc., are done by the furnace crew without loss of operating time.

OPERATING DETAILS

Operations are conducted on a 24-hr. cycle basis divided as follows: 8 hr. for charging (and partial melting), 2 hr. to complete melting, 5 hr. for refining (skimming and oxidizing), 3 hr. for poling and from 4½ to 6 hr. for casting.

The charging crew operates on the afternoon shift. Their duties consist of seeing that the furnace is properly charged and partly melted. The charging is done entirely by hand; that is, transveyor skids are spotted adjacent to the furnace and charging paddle and the pieces of scrap, weighing approximately 100 lb., are manually removed from the transveyor skids and placed on a long I-beam paddle which is suspended on a trolley located directly on the center line of the furnace side door. The loaded paddle is pushed into the furnace and by a slight twist of the paddle the scrap is allowed to fall off.

Skill is required in placing the scrap in the furnace so that it will be melted down quickly enough. In melting scrap it is desirable that the scrap be placed directly in the flame, because in this type of charge there is considerable dead air space between the pieces of copper. These dead air spaces act as insulation and the heat for melting must be largely supplied by direct contact with the flame. It is for this reason that heavy scrap is much more easily melted than light scrap wire; likewise, quicker melting can be obtained by using more than one burner.

The refining crew operates on the night shift. This crew conditions the charge and begins the poling. Shortly after the charge has come afloat it is skimmed while the slag is still viscous enough to be removed easily. A sample of the copper is taken for immediate analysis to guide the subsequent refining operation. The copper oxide scale is thrown into the furnace at this stage and is sprinkled over the surface to facilitate its mixing with the charge. If the scale is thrown in all at once in one place it is difficult to melt, and copper losses will increase because some scale will be skimmed off with the slag. After the scale is added the charge is thoroughly blown with air through a $\frac{1}{2}$-in. iron pipe from a 15-lb. pressure air line.

Oxidation with skimmings as necessary to remove slag and provide a clean metal surface is continued until a sample button taken from the charge shows a distinct brick-red cubical fracture. At this point the charge contains from 0.8 to 1.4 per cent. oxygen (7 to 12 per cent. Cu_2O). If samples taken approximately every two hours show the lead content to be more than 0.005 per cent. the heavier oxidation is approached. If, however, the lead content is low the lighter oxidation is satisfactory. When the lead content has been reduced and a satisfactory oxidizing button sample obtained, the charge is held for at least 1 hr. and then is skimmed clean. The poling operation is immediately begun by the refining crew.

Poling the Charge

The poling operation usually requires approximately 3 hr. and the burning of at least eight green hardwood poles. The poles used are largely maple and birch; they are each approximately 10 in. dia. at the

butt, at least 20 ft. long, and weigh approximately 200 lb. Maple is preferred because it burns more slowly than other woods. During poling the usual test buttons are taken to determine when the oxygen has been reduced to from 0.03 to 0.06 per cent. At this oxygen content the copper is considered satisfactory for casting and this oxygen content, as determined by the set surfaces of the wire bars, is maintained during casting by poling through the side door as required. The set surface of a wire bar should be level or slightly convex, never concave.

Casting Bars

From 4½ to 6 hr. is required to cast the heat of wire bars, two operators dipping alternately. The casting crew consists of these two operators, an operator to tend the furnace and to keep a brand in place to hold back

FIG. 3.— CASTING WIRE BARS.

the charcoal on top of the metal bath so that the ladles may receive the molten copper from a clean metal surface, another to spray the molds, another to dump the wire bars from the molds into the cooling water after solidification, and two others to remove the bars from the cooling tanks— seven in all.

The wire bars average approximately 250 lb. in weight. They have approximately the same cross-section as the A. S. T. M. standard 225-lb. bar; that is, they are 4 in. wide at the top, tapering to 3½ in. wide at the bottom, and are 4 in. high. However, they are 60 in. long instead of the 54 in. as specified by the A. S. T. M. requirements. The length was

increased in order to obtain a heavier wire bar which could still be rolled by the same reductions that are applied to a standard 225-lb. bar.

The poled-to-pitch metal is hand-dipped from the front door of the furnace, using 18-in. dia. cast-steel ladles supported on a round steel handle shank approximately 10 ft. 6 in. long. The ladle and shank are supported from the trolley by means of a hook which fits into a link around the ladle shank. The shank is thus made removable and can be changed easily from the trolley serving the four molds on the one side of the casting area to the trolley serving the four molds on the other side. The ladle is equipped with pouring lips on each side, thus allowing the operator to pour at will from either side and avoiding the hazard of a 180° turn with a ladle full of molten metal. Pieces of charcoal placed in the ladle to prevent oxidation of the copper during pouring are held back by means of dams cast into the ladle on the bowl side of the pouring lip.

A protective coating of approximately $\frac{1}{16}$ in. of refractory cement is applied over the entire surface of the ladle and allowed to dry thoroughly before the ladle is placed in use. This retards "burning" of the steel by the hot copper and also prevents the copper from freezing tight to the ladle. Two ladles are used to dip each furnace charge. The first half of the charge is dipped with one and the second half with another. With this sort of use, a ladle can be used approximately two weeks before it gets so badly out of shape that ordinary hammering cannot reshape it.

Molds for Wire Bars

The molds used are made of copper and are cast at the refinery. They are made by filling a steel box with tough pitch copper, then forcing a solid steel core into the molten metal and allowing the metal to solidify around the core. When the core is withdrawn its impression remains in the mold. Eccentric lugs cast on each end are used to support the mold in a horizontal and upright position on the cooling water tank without tipping over. A steel pipe insert cast in one end of the mold is the socket for the rod used in turning the mold over to dump the solidified wire bar into the water. During the casting operation 3 or 4 in. of the bottom of each mold rests in water, thereby allowing heat to be conducted from the mold to the water and increasing the life of the mold.

The life of a mold is erratic and depends largely on the care given it; that is, whether or not it is kept cool during use. The mold temperature should be about 250° F. when ready to receive the copper and should be kept as close as possible to that temperature all during the casting operation. This means that the molds should be well protected with a good wash, that the metal being cast should not be too hot, that the wire bars should be freed from the molds as soon as they are set, that the bottoms of the molds should rest in water, and that the molds should be cooled

back to 250° F. as quickly as possible. Given such care, our molds have an average life of 4000 to 5000 bars.

A satisfactory mold wash is bone ash mixed with water in the proportion of one part bone ash to one part water by weight. The bone ash should be fine, at least 97 per cent. to pass a 200-mesh screen. It should be applied on the warm mold with an air spray gun, not a brush. A spray gun of the type used for spraying lacquer finishes has proved satisfactory. A test of a good mold washing is that it will not allow a side splash or a small shot of metal to freeze to the side of the mold but will cause the metal to fall back into the mold.

A suitable temperature of the molten metal for hand-casting is approximately 2060° F. At this temperature the metal will pour freely and will fill out the mold well. Colder metal will make hand-dipping very difficult because of the quick formation of a heavy skull on the ladle. Much hotter metal will cause undue consumption of both ladles and molds.

Consumption of Various Materials

The figures on consumption of some of the various materials at the refinery are as follows: The fuel-oil consumption is approximately 1300 gal. daily, which calculates to approximately 30 gal. per ton of copper melted. Approximately 10 green poles weighing 200 lb. each are required to pole the heat of oxidized copper to the required pitch. An additional 15 smaller poles weighing 100 to 200 lb. each are required to maintain the copper at pitch during casting. This calculates to a pole consumption of approximately 100 lb. of wood per ton of copper. To maintain a blanket of charcoal on the bath during casting requires approximately 1000 lb. of northern body wood charcoal. Water for cooling the bars is used at the rate of 250 gal. per min. (125 gal. to each tank) during the casting period. Approximately 60 lb. of bone ash is required to spray the molds for casting 350 bars. From 30 to 50 ft. of ½-in. black iron pipe are used in oxidizing each charge unless the refining is prolonged to reduce the lead content, when as much as 100 ft. may be used.

Over a period of approximately three years, the material shrinkage, or the difference between gross weight of secondary copper scrap input and wire-bar output, has averaged approximately 2 per cent., over one-half of which was recovered from the slag produced.

IMPURITIES AND THEIR ELIMINATION

The impurity most frequently found in the copper charges at the Hawthorne plant is lead. This is unfortunate, because lead is one of the hardest elements to remove from copper by fire-refining methods.

There seems to be some question as to the effects of lead in copper.[2] Experimental evidence at the Hawthorne plant indicates that small amounts of lead, for example up to a maximum of 0.015 per cent., will cause no trouble during hot-rolling into wire rod or while the rod is being cold-drawn into heavy sizes of wire. Neither does it have an appreciable effect on the tensile strength or elongation of the cold-drawn wire or on the electrical conductivity of the wire after anneal. However, if copper containing between 0.005 and 0.015 per cent. lead is processed into fine-size wire—for example, smaller than No. 22 B. & S. gage—which is to receive a subsequent low-temperature anneal, it has been found that the lead has a retarding effect on the anneal. For this reason all W. E. brand copper for general release to the rod and wire mill must have a low lead content.

Maintaining this low lead content is one of the refinery's principal problems. Supervisory effort is directed definitely toward keeping it out of the raw material entering the charges but if this fails, as it does occasionally, attempts are made to remove it by fire-refining methods. If the analysis obtained on the melting-down sample shows more than 0.005 per cent. lead present, approximately 100 lb. of lime rock and 100 lb. of sand is added to the furnace after the charge has been rather thoroughly oxidized. The resulting slag is allowed to remain on the charge for at least an hour, during which time the bath is continually blown with air. Samples are taken from time to time to determine the progress of the lead removal. This method of slagging is continued until the lead has been reduced to a satisfactory content.

Lead removal is considered to be a direct function of the mixing; that is, effort must be made to mix the charge thoroughly while it is in the oxidized condition, so that each part of the charge can come in contact with the slag. Entirely satisfactory results are seldom attained because of the impossibility of thoroughly circulating the complete metal bath in the limited time usually available. If the lead content starts rather high, say around 0.1 per cent., it may rather readily be reduced to as low as 0.01 per cent, but to reduce 0.01 per cent. to less than 0.005 per cent. is more difficult than to accomplish the complete first-mentioned reduction. Some actual lead reductions accomplished are shown in Table 1.

Sulfur is sometimes found as an impurity in the copper. It is evidenced at the beginning of casting by "gassy" copper and the characteristic "overpoled" surface of the wire bars. The fuel oil at the refinery contains less than 0.3 per cent. sulfur but it is the opinion, as yet unconfirmed, that such cases of sulfur in the copper are due to allowing unburned fuel oil to fall on the surface of the metal bath either after or immediately before poling has commenced. Therefore care is taken

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[2] N. B. Pilling and G. P. Halliwell: Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper. *Trans.* A. I. M. E. (1926) **73**, 679.

to see that sufficient air is supplied to the burners to completely atomize the oil at all times, and that when closing the oil burners the oil supply is turned off before the air supply. In a case or two where the "over-poled" condition has not been very bad, the charge has been oxidized back slightly and a satisfactory quality charge of metal produced. Such a procedure is decidedly not advisable. The only safe thing to do is to oxidize the whole charge back to at least a columnar fracture button (containing approximately 3 per cent. Cu_2O) and re-pole the charge.

TABLE 1.—*Lead Reductions Accomplished*

ORIGINAL LEAD CONTENT PER CENT.	REDUCED TO PER CENT.	HOURS
0.015	0.003	7
0.030	0.003	9
0.041	0.005	$9\frac{3}{4}$
0.059	0.012	12
0.076	0.014	$12\frac{3}{4}$
0.092	0.012	15

Silver is occasionally found as an impurity. Most likely it occurs through the melting down of some high-silver copper wire which was in use as line wire before the electrolytic refineries were as numerous as they are today. No attempt is made to reduce the silver content in the Hawthorne refining furnace and such heats are not cast into wire bars for general release in our rod and wire mill.

A peculiar impurity, or possibly it should be considered a condition, is noted when melting down junked wire obtained from localities near the oceans. The weathered wire is coated with a salt which is probably copper chloride. Whatever the material is, it has no effect on the quality of the final product.

Impurities other than those mentioned are seldom present. Iron would be if it were not so easily removed during the oxidizing period, because tramp iron is present in all scrap. Antimony and arsenic may be present in small amounts but they are always less than 0.003 per cent. on the final material without taking any special steps to remove them.

CONCLUSION

Four years of experience have resulted in the assurance that wire bars of present commercial electrolytic quality can be made by converting secondary copper in a suitable reverberatory furnace. It is true, however, that the secondary copper must be selected carefully and impurities kept out of the final product largely through the careful control of the input. Whether or not it is economical to recover secondary copper as wire bars depends on the amount of selected scrap available, the cost of the scrap, the market for the wire bars, and the relation of the proposed location of the installation to both the source of the secondary copper and the market for the wire bars produced. It is impossible to give a general

statement as to the minimum size of an installation that could be operated on an economical basis without taking into account many factors, including freight rates. A study of each individual case must be made in order to determine the advisability of installing such a process.

ACKNOWLEDGMENT

DISCUSSION

T. A. WRIGHT, New York, N. Y.—In connection with this secondary metal symposium, the secondary values for 1928, which have just been released by the Government, are of interest. They are: Copper other than brass, $93,600,000 and over; brass scrap remelted, $70,935,200; lead, including alloys of various types, $38,-797,200; zinc, $10,162,600; tin as metals and alloys and chemical compounds, $35,678,-300; antimony, $2,451,400; aluminum as metal and alloys, $22,848,400, and nickel, $3,150,000; a total of $277,623,500 for 1928 as against $256,352,000 in 1927. It shows the tremendous importance of these metals in our economic system.

J. W. SCOTT.—The title of our paper might have been amplified to read The Manufacture of Wire Bars from Secondary Copper at the Hawthorne Works of the Western Electric Co., because it is really a more or less particular description of the process as carried on at Hawthorne.

As Mr. Wright has suggested, the importance of secondary copper is becomngs greater and greater, and the papers in this symposium will bear him out. The pictiure he did not give is that in 1927 for each pound of new copper mined in the United States there was approximately one-half pound of secondary copper reclaimed for re-use.

Most wire bars are made from primary copper. The ore, of course, is smelted and blister copper is obtained. The blister is melted in an anode furnace and then cast into anodes which are placed in a refining cell to be electrolytically deposited as cathodes. In refining cells practically all of the metallic impurities are eliminated, so that when the cathodes are melted in the cathode furnace very little refining other than an oxygen-content control is given the copper. Practically the entire output of the country is made in this manner.

The Western Electric Co. is making satisfactory wire bars from secondary copper, although a wire bar is one of the shapes requiring the purest copper. A wire bar must of necessity be pure because it must meet rather stringent requirements. It must have a high electrical conductivity, and lend itself to all working conditions imposed on it in the rod and wire mill. The wire, after it has been made in the wire mill, must respond readily to the annealing conditions, because copper is generally used in the annealed condition. We attribute our success in maintaining high-quality copper wire bar production from secondary copper to five different factors:

1. The scrap is carefully classified and sorted. Scrap copper is just what the name implies. It is likely to have any impurity in it. There is no reason why that impurity should be added to the furnace, and it is much simpler to remove it before than after the scrap goes into the furnace.

2. The furnace is constructed properly for the refining of secondary copper directly into wire bar quality copper. We use a magnesite side-wall construction in preference to silica brick or sand because we believe that magnesite has a longer life and also reduces the amount of impurity which might be absorbed by the wall. Once a furnace is salted, even slightly, it is difficult to make a good charge of copper without taking corrective steps.

Our furnace has two burners. We feel that the number of burners is a function of the amount of scrap to be melted. Melting scrap is somewhat different from melting cathodes. Scrap always has considerable dead air space between the strands of wire which acts as an insulating medium. In order to melt the copper quickly the effect of the dead air must be neutralized through direct contact of the wire with the flame. Therefore it is advisable that more than one burner be placer on furnaces used to melt copper wire if quick melting is desired. Also, the manner of operation of our burners permits close control of the production of combustion which is a function of the draft conditions and the type of fuel used. We use oil with very low sulfur content.

3. The charge is heavily oxidized during the refining—to at least 0.8 per cent. oxygen and sometimes as high as 1.4 per cent.—before poling back is begun. Within this range the copper is in a condition evidenced by a cubical fracture button. We feel that heavy oxidation allows thorough scorification of the charge and will act as a factor of safety should some unwanted impurity have entered the charge.

4. We operate on a careful chemical control basis. Each charge is analyzed when it is melted down, and chemical analyses govern the refining operation throughout the refining cycle. The charge is not poled back until we are sure that the material will be satisfactory material on the completion of the poling operation.

5. The process receives very close technical supervision.

We cannot indicate the minimum size of installation that could be used to manufacture copper wire bars from secondary copper at a profit. Too many things must be included in arriving at such a statement. A complete economic study, involving several factors, must be made of each case. However, if there is a sufficient supply of clean scrap available, and if the cost-study man shows that it is economically feasible to convert the scrap into wire bars, one may be reasonably sure that wire bars of satisfactory quality can be produced.

A. T. MARCH, Chicago, Ill. (written discussion).—Until 1923, all Bell system scrap copper, including process scrap, at the Hawthorne plant of the Western Electric Co. was being sold, excepting a small amount that was used in the Hawthorne foundry for copper-alloy castings. A study of the situation indicated that it would be profitable to convert this copper into wire bars at Hawthorne and accordingly it was decided to install a small experimental fire refinery with the following objects in view:

1. To determine whether electrolytic quality wire bars could be produced from secondary copper by fire refining only.

2. To determine what secondary copper was suitable as a source of raw material for converting into wire bars of accepted quality by fire refining.

3. To obtain first-hand operating experience in the fire refining of secondary copper, which would be invaluable if it was desired to proceed with the project.

This experimental furnace was 4 ft. long by 3 ft. wide inside and had a maximum hearth depth of 1 ft. 8 in. and an average depth of 1 ft. 6 in. The bottom was an inverted arch of 12-in. silica wedge brick resting on an inverted arch of 9-in. wedge firebrick. The roof was 9-in. wedge silica brick. Both the top and bottom silica arches were built to a 3-ft. inside radius. The sides were 18 in. thick, 9-in firebrick on the outside, completely lined with 9-in. magnesite brick.

The fuel was a 300 B.t.u. blue water gas. Oil would have been preferred but would have required a special installation whereas gas was available in the building. The

capacity was a little over 4 tons and the daily output of wire bars around 2 tons.   The wire bars thus produced compared favorably in rolling and drawing properties with wire bars received from the electrolytic refineries, thus indicating that wire bars of electrolytic quality could be produced from selected secondary copper by fire refining.

While we found that it was possible to reduce the lead content of copper by fire refining, our results indicated that it was not economical to do so.   Further, the salting of the ceramic lining of the furnace with lead renders the removal of lead doubly difficult if lead-bearing copper is refined continuously and, moreover, makes high-lead heats out of subsequent charges of lead-free material.

On the basis of the results obtained from operating the experimental furnace the present installation as described by Mr. Scheuch and Mr. Scott was designed and placed in operation in 1925.

S. SKOWRONSKI, Perth Amboy, N. J.—The common practice of flapping and poling the copper is continued.   Time and time again people have tried to remelt copper without flapping and poling, and always have failed.   They may have been fairly successful on the first remelting, but on the second and the third remelting, it is invariably a failure.   The poling and flapping operations must be used to produce satisfactory copper.

W. R. WEBSTER, Bridgeport, Conn.—This paper is of particular interest because it shows the high degree of perfection attained in an art by purely empirical methods long before there was any science of metallurgy.   It also illustrates the extremely circuitous means of arriving at a result involved in the present practice of copper refining.   As a matter of fact, the term "refining" is somewhat of a misnomer as far as the purpose achieved in the installation described in the paper is concerned, in that the raw material involved is less pure than the product only by accident, and barring such accident it must still be employed for but a single purpose, namely the attainment of a condition of gaseous equilibrium requisite to prevent blowholes on the one hand an unequal shrinkage and consequent piping on the other.

Contrast this 24-hr. process with that of the open-hearth furnace in which a charge of old stoves, automobiles and railroad iron, sweetened with a little pig, is in 8 hr. made into first-class steel ingots.

The fact that in spite of the progress in other branches of copper metallurgy, which has brought to the refining furnace a product which is to all intents and purposes chemically pure, this clumsy, inefficient, contaminating and time-consuming process, originally devised for quite a different purpose, is still necessary for the production of a usable casting, is a distinct and unqualified challenge to the science of metallurgy.

Utilization of Secondary Metals in the Red Brass Foundry

By H. M. St. John,* Detroit, Mich.

LIKE every present-day manufacturer, the brass foundryman is faced with the necessity of reducing the cost of his finished product without impairing its appearance or quality. He must use every economy that the progress of art and science puts at his disposal and should also be alert to profit by any peculiarity in his own situation or the nature of his product that may give him an exceptional advantage.

Much can be accomplished by the adoption of labor-saving equipment and improved methods of melting, molding and handling. Control of pouring temperature, study of defective castings and their causes, laboratory control of molding sand and core mixtures, the use of less expensive alloys, all contribute to the desired end. Assuming that the composition of the alloy is already as inexpensive as the character of the casting will permit, still further savings can be made by the intelligent purchase and utilization of the metals needed to produce the desired analysis.

FUNCTIONS OF SECONDARY AND VIRGIN METALS IN CASTING BRASS

It is no longer a general assumption among foundrymen that quality castings must be made from an "all virgin" mix. If suitable secondary metals can be obtained more cheaply it is wasteful to use any larger proportion of virgin metal than is required to produce castings of the desired properties. To follow such a course, however, imposes upon the foundryman a heavier obligation than was formerly the case, to make sure by test and inspection that his castings really are of the desired quality. So long as he used the most expensive grades of metal and his melting practice was reasonably correct he was not obliged to give much thought to the quality of the metal in the castings. If he is to use secondary metals he must, in order to retain the confidence of his customer, examine these metals very carefully before use, exercise scrupulous control over his melting and pouring conditions and examine his castings closely.

These statements apply more particularly to the jobbing foundry. The foundry department in a manufacturing plant is in a somewhat

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more favorable position with respect to competition. However, a saving made in the foundry is a saving in the cost of the finished product, regardless of whether castings are purchased or made at home, and there is no good reason why the foundry department should not operate as economically as a jobbing foundry; in fact, there are a number of reasons why the foundry department is in the best possible position to make a maximum use of secondary metals. For one thing, other departments of the same plant are frequently a convenient and reliable source of supply for some of these secondary materials, which would otherwise have to be sold to a dealer. Then, too, when the foundry's customer is under the same roof, the behavior of the castings as they pass through the shop can readily be observed and any defects in the metal can quickly be determined and corrected, without loss of business or fatal damage to the foundry's reputation.

An important reason for using a certain proportion of virgin metal in the foundry mix is to obtain a high degree of fluidity in the molten metal, or give the metal "life," so that intricate shapes can be poured without misruns, and uneven shrinkage due to sluggish metal may be avoided. This is principally a function of the new copper. There are other means of enhancing fluidity, such as the addition of phosphor copper or other deoxidizers, the use of a small percentage of nickel, etc. The method of melting also has a bearing on this problem and it is rather likely that the increasing use of electric furnaces has diminished the brass foundry's virgin-copper requirements. If the necessary degree of fluidity can be maintained without the addition of virgin metals, there seems to be no good reason why secondary metals should not be used, provided, of course, that these contain no directly detrimental impurities.

As a matter of fact, secondary copper, lead and zinc are extensively used by red brass foundries. The percentage of tin in the alloy is commonly so small and its influence so important that the use of secondary material, even if readily obtainable, is not so profitable as to make the practice common. However, a good quality of high-tin turnings can often be used to advantage in the production of castings having a lower tin content.

Selection of Scrap Available for Brass Foundry

It may be assumed that almost any foundry puts back into its furnace charges gates, sprues, scrap rough castings and miscellaneous heavy metallics resulting from its own operations. A foundry department will also handle in the same way scrap castings and turnings from the plant's own shops, while a jobbing foundry often has an agreement with its customers by which it receives for credit scrap castings and turnings from its own product. These materials should offer no difficulty in a

well operated foundry. Other secondary materials available for use may be listed as follows:

1. Secondary elemental metals, such as copper, tin, lead and zinc.
2. Composition ingot.
3. Composition turnings.
4. Composition scrap castings.
5. Composition wrought metal, such as clippings, rod ends, etc.

6. Buffings and grindings.
7. Ashes, slag, skimmings, etc.
8. Foundry floor sweepings.
9. Washings or concentrates.

The successful use of secondary elemental metals is more a matter of visual inspection coupled with good judgment than it is of chemical analysis. For this reason there is a considerable advantage in purchasing metal in its original scrap form rather than in a remelted form. Inspection of such scrap affords valuable information as to its past history. Copper mill scrap, such as busbar ends and the like, or scrap resulting from the fabrication of rolled or drawn copper can readily be identified as of good quality. An examination of cabbaged wire, or cable from which insulation has been removed, will usually reveal whether the material has been properly sorted and handled in such a way as not to damage its metallurgical qualities. Care should be taken to determine that copper scrap of this nature is clean, free from grease, insulating materials and other non-metallics, and reasonably free from solder. Cabbages that may contain hidden iron can be detected by sprinkling them with salt followed by water and allowing them to stand for a few hours. Lead in the form of cable sheathing or clean lead pipe is likely to be of satisfactory quality. Zinc in its original scrap form is sometimes but not so frequently obtainable.

The remelting of scrap metals destroys most of the evidence regarding their past history. In purchasing such remelted—and presumably refined—metals the foundryman should be guided by the reputation of the smelter and his own past experience with the source of supply. Chemical analysis for impurities is of some guidance to the experienced metallurgist but so little is definitely known regarding the influence in brass of the various impurities that are likely to be in scrap copper, lead or zinc that it is practically impossible to write a useful chemical specification. The user must be governed by the results he obtains under his own conditions of use.

PURCHASE OF COMPOSITION INGOT

In the purchase of composition ingot, specification and test by chemical analysis can be used to some advantage, largely because the proportion of impurities is higher. It remains true, as with the elemental

metals, that the influence of these impurities is not well understood and that some of the most important, such as dissolved oxides, for example, cannot readily be determined by analysis, but the relative proportion and character of the impurities present in the ingot are frequently a valuable indication as to the nature and grade of the scrap materials used in its manufacture. If specifications are imposed which are rather exacting without being unreasonable the ingot manufacturer must select his materials with care and use good practice in their manufacture. The result is likely to be good ingot. This general effect, rather than the control of individual impurities, is the principal object to be gained by the use of purchase specifications. If, by some mischance, the ingot maker does make a substandard batch of ingot it will go to a heedless customer.

One such specification which has been used successfully in purchasing millions of pounds of composition ingot is as follows:

	Not Less Than Per Cent.	Not More Than Per Cent.
Copper	78.0	80.0
Tin	1.50	2.50
Lead	6.25	7.75
Zinc	11.00	13.00

IMPURITIES

	Not More Than Per Cent.
Iron	0.30
Bismuth	0.05
Antimony	0.15
Arsenic	0.25
Aluminum	None
Sulfur	0.05
Phosphorus	0.05

Total impurities exclusive of nickel not to exceed 0.50; nickel up to 0.50 not to be classed as an impurity. For convenience, total impurities may be defined as the difference between 100 per cent. and the sum of the copper, tin, lead and zinc (plus nickel up to 0.50).

SELECTION AND TREATMENT OF TURNINGS AND BORINGS

Among the alloyed materials that may be purchased, the most important is composition turnings or borings. If sufficiently clean and of suitable analysis these may often be used directly in the foundry melt along with brass turnings produced in the plant's own machine shop. Otherwise they form a convenient material for the manufacture of ingot. The proportion of oil, moisture, free iron and solid non-metallics in the turnings should be carefully determined and their presence allowed

for in calculating the price which the foundry can afford to pay. The turnings should be analyzed and rejected if they contain aluminum, either free or combined, unless the foundry is in a position to remove the aluminum by refining. Other impurities, in reasonable amount, can be taken care of in the ingot-making process.

Practically all brass turnings contain some free iron and many carry appreciable percentages of oil and moisture. The iron should be removed by passing the turnings through a magnetic separator, which every foundry should possess for the treatment of turnings from its own shop or from its customers. A variety of dryers, commonly home made, are used for eliminating oil and moisture. One type of dryer, recently placed on the market, conveys the turnings through a furnace chamber heated by gas burners so adjusted as to avoid entirely an oxidizing atmosphere within the furnace. The oil is removed largely by distillation and to some extent the vaporized oil is burned within the furnace to supplement the heat supplied by the gas burners. Completely dry turnings, comparatively free from surface oxidation, can be obtained cheaply in this manner. If the turnings are eventually to be melted in an electric furnace, complete removal of oil is of the utmost importance.

Rod-brass turnings, particularly if available within the plant, may profitably be used by the foundry. These should pass through a centrifugal dryer before leaving the screw machine department, after which their oil content should not exceed 1.5 to 2.0 per cent. This residual oil may be removed in a furnace dryer. After passing through a magnetic separator, the turnings are ready for use. If the drying is carried out so as not to oxidize the surface of the turnings appreciably, they are entirely suitable for use directly in the foundry melt, with a corresponding saving in the amount of composition ingot used.

Utilization of Composition Castings and Wrought Metal

The utilization of composition scrap castings is a matter requiring specialized experience and skill. The analysis of this class of material is subject to infinite variation and there is no adequate method of sampling without first melting. Scrap castings should be carefully sorted and classified before melting; even then it is easy to go wrong. For this reason such miscellaneous scrap is not suitable for foundry use.

Composition wrought metal, whether in the form of clippings, punchings, etc., or worn-out metal articles such as automobile radiators, can be purchased of uniform composition and such material may often be used economically. Its successful use is a matter of good judgment and careful inspection. The presence of free iron should be avoided because the magnetic separator will not handle this material. Allowance should be made for the presence of solder, which should not be excessive.

TREATMENT OF LIGHT AND SMALL SCRAP

The ashes, slag, skimmings, etc. produced by the foundry should be crushed and concentrated. A convenient method is to put this material through a ball mill that discharges its fines directly to a Wilfley table or similar device. The coarse metal that will not pass through the trommel of the mill may be used directly in the foundry melt or in the ingot-making furnace. The table can be adjusted so as to recover practically all of the metal from material of this class. The table concentrate, averaging 80 to 90 per cent. metallic, is ready for ingot making as soon as it has been through the magnetic separator. The middlings, usually less than 50 per cent. metallic, should be fed back to the table for retreatment.

Foundry floor sweepings, containing the metal which has been spilled and spattered during the pouring of the molds, can advantageously be screened dry, before concentration by a wet method. A two-deck vibrating screen, using 10 or 12 mesh on the upper deck and 30 to 40 mesh on the lower deck, will separately deliver two concentrates, the coarser of which should assay 75 to 85 per cent. metallic and be fit for ingot making without further concentration. The finer concentrate, averaging about 50 per cent. metallic, should go to the ball mill and table for additional treatment. The fine molding sand, which has passed through the 40-mesh screen and is almost free from metal, can often be blended with raw molding sand for return to the foundry heaps. The vibrating screen should be enclosed and equipped with a fan and dust collector; this not only avoids a serious dust nuisance but also removes the extreme fines, which would tend to make the salvaged molding sand too close for successful use in the foundry.

These statements refer only to such materials as originate in the foundry or in the plant of which the foundry is a part. It does not pay to compete with the smelter in the open-market purchase of such small scrap. Occasionally, perhaps, but rarely, it may be worth while to buy rich concentrated material of known composition from outside sources.

Buffings and grindings that originate in the plant may satisfactorily be used in the foundry department. If richer than 60 per cent. in metal content, they can be used directly in ingot making; if leaner than 60 per cent., it may be necessary to concentrate them on the Wilfley table, and in this case they should go through the ball mill first, not for grinding but to be thoroughly mixed with water. Even when wet the metallic particles in buffings and grindings are so finely divided and so light that a large proportion will find their way into the table tailings. Wasteful as this may appear, it is usually more economical than to dispose of the material by sale to a smelter.

Ingot Making in the Foundry

In many cases the foundry, particularly the foundry department of a manufacturing plant, can profitably produce composition ingot for its own use. This does not mean that the foundry can economically compete with the secondary smelter and refiner in collecting and refining miscellaneous scrap materials and metal-bearing wastes of unknown composition. It does mean that an establishment producing within its own walls substantial quantities of scrap materials and metal-bearing wastes which it would otherwise sell to the junkman or the refiner can frequently make use of these materials, supplemented if necessary by secondary metals of known composition and definite character purchased on the open market, to manufacture composition ingot of good quality for use in its own foundry. As the ratio of metal purchased outside to the metal originating in the plant increases the operation usually becomes less profitable.

The ingot-making department should be a separate division of the foundry. Furnaces used in regular foundry production should not be employed for this purpose. Almost any hearth-type of furnace may be used, provided its melting chamber is comparatively large and readily accessible for slag-skimming purposes. The rocking arc type of electric furnace has some advantage in that it keeps its charge agitated and, by virtue of its neutral atmosphere, recovers most of the zinc, which would be oxidized in a fuel-fired furnace. It also lends itself to certain very effective refining methods that cannot be carried out so well in conjunction with oxidizing atmospheres and stationary baths.

Materials available for ingot-making charges will normally consist of rich concentrates, both wet and dry, buffings, grindings, rod-brass turnings, clippings and other wrought brass or bronze scrap and composition turnings purchased from outside sources. These materials should be blended in such proportions as to produce an ingot of analysis which can conveniently be used in the foundry. It is not necessary that the ingot should have exactly the composition of any of the foundry alloys—this would often require the addition of copper and other elemental metals which can more effectively and economically be added to the ingot when the latter is remelted for use in the foundry—but the ingot should be of such composition that it can be used for the production of the foundry alloys without adding excessive amounts of new metals.

The charge going into the ingot-making furnace should contain no free iron and should be free from oil or, in the case of the electric furnace, any other material that will leave a carbonaceous residue. Not more than 20 per cent. slag-forming material should be included in any charge. In other words, the charge should not contain too large a proportion of comparatively low-grade concentrates, buffings or grindings.

Depending on the quantity and character of the non-metallic materials in the charge, a varying amount of a fusible alkaline flux should be included with the charge. The author prefers. soda ash. Borax or fluorspar can be used. The object is to make the siliceous slag sufficiently soft so that it may be skimmed readily, without making it soupy. A pasty slag, which breaks off in chunks when it is pulled from the furnace, is just right. The skimming operation should be performed through a wide-open furnace door, using a long-handled hoe with a steel handle fastened to the center of the head, so that the hoe has four corners which can be used to clean out corners of the furnace chamber.

REFINING IN THE ELECTRIC FURNACE

The refining of impure non-ferrous metals in the electric furnace is a fascinating subject with many unexplored possibilities. It is known that both aluminum and combined iron can be wholly or partly eliminated by the use of an alkaline sulfate, such as anhydrous sodium sulfate, or an alkaline earth sulfate such as barium sulfate. In either case the action is the same, the sulfate acting as a selective oxidizing agent and attacking the more readily oxidized metals, while leaving the others, even the zinc, relatively unaffected. These fluxes can best be added to the molten metal in the furnace after skimming. The amount of refining done depends on the quantity of flux used, the temperature of the metal and the amount of time allowed after adding the flux. The use of an additional quantity of flux in the ladle when the metal is poured is of some benefit.

The brass will usually pick up some sulfur from a sulfate flux. This is commonly of little importance but may at times be injurious. The percentage of sulfur can be diminished by the use of soda ash in the ladle just as is sometimes done in the removal of sulfur from cupola-melted cast iron.

In the neutral atmosphere of an electric furnace the presence of finely divided carbon, originating from oil, for example, will result in the reduction of metallic silicon from the siliceous slag or from the furnace lining. Silicon is an injurious impurity in red brass, even when its percentage is 0.05 or less. It should be avoided but if present can be removed by the use of barium sulfate or sodium sulfate.

DISCUSSION

T. A. WRIGHT, New York, N. Y.—Automobile radiators are coming into consideration. There are about four types of partly prepared radiators; that is, four classes such as sweated radiators from which the iron has been removed. One runs about 56 per cent. copper and another about 66 per cent. One lot I have in mind, 1000 tons, say 30 cars, did not vary over 0.5 per cent., running 74 per cent. copper. Then there is the radiator that will run around 83 or 84 per cent. copper. The tin in

those will run from 1.2 to 5 and 6 per cent., and in the low tins the lead will be in an equivalent amount. Certain secondary smelters and dealers are processing those radiators and briquetting them. They come in a very convenient form, and outside of scale and a little bit of iron that may be in them once in a while, they are fairly clean material.

W. F. GRAHAM, Mansfield, Ohio (written discussion).—The writer of this paper apparently has not made a definite distinction between secondary metals and scrap materials as a base for melting in the red brass foundry. The designation of scrap materials should apply to miscellaneous metals and alloys which, either from their physical nature or lack of uniformity and impurity of composition, cannot be used to make the product without affecting the resulting quality. The secondary metals and alloys would be those that have been refined or smelted from the scrap materials and can be used directly. The writer has interwoven the discussion of the use of secondary materials, such as composition ingot, with that of the use of miscellaneous scrap, and also the process for producing secondary materials from the scrap.

A large industry has grown up in recent years based on the need of collecting, classifying and refining scrap non-ferrous materials and putting them in such form that they may be usable by the brass-foundry trade. On the basis of the fact that there is an industry which seems to be a necessary part of the scheme of things, the writer's assumption is rather questionable. In general, the utilization of scrap materials by the foundry or the operation of a refinery as an adjunct can not be performed economically. There may be foundries which, either from their location or by their connection, are in a position to obtain scrap materials in sufficient quantity and uniformity and high enough in quality for their purposes.

As industry progresses, undoubtedly there will be larger quantities of non-ferrous materials revolving through the cycle of producers to consumers and back again to producers. There must be a well organized, definitely set up system of collecting, sorting and refining these materials in order to conserve our natural resources.

I have no doubt that any well organized foundry with some technical direction can properly handle scrap materials from the standpoint of producing a satisfactory melting base for their operations. This should be approached also from the side of final cost and efficient functioning of the organization. The question as to whether scrap materials can be purchased as economically or more economically by the foundry than by the secondary metal producers should be given a great amount of consideration.

The organization of every secondary metal producer is keyed up to a high degree in its purchase of scrap materials. It is unnecessary for me to call attention to the complicated but efficient aspect of this part of the business. In respect to the technical side, which has to do with the handling and sorting of the scrap materials and refining them into usable form for the brass foundry, it is the writer's opinion that while there is considerable room for improvement in the methods in the view of modern practice of materials handling and furnace operation, they do produce the result. We buy many carloads of composition ingot in a year, and our rejection on analysis is nil.

As regards the use of secondary metals in the brass foundry, it is my feeling that properly refined and alloyed materials produce better results than virgin mixes. I believe that no foundryman need worry at all about the use of secondary metals from the standpoint of quality, and in this respect I heartily agree with the author of this paper.

I do not agree with the author that it is an economic procedure for a foundry organization to use miscellaneous scrap materials or to produce secondary materials as a base for their melting operations. If scrap materials are used without previous production of secondary ingot, the quality will always be in question. In either

case, the ultimate cost by reason of the use of these materials will be above that resulting from secondary metals purchased from the refiners in a condition ready to use in the brass-melting furnaces. It would seem that the old saying, "A shoemaker should stick to his last," has a very definite application in this connection. While undoubtedly cost figures can be cast up to make the former procedure seem possible, there are other factors of a more or less intangible nature entering into this procedure.

I comment on this matter from the standpoint of the operation of the average foundry, producing a high-quality product, and not to the exceptional circumstance.

T. A. WRIGHT.—I would like to point out two terms the use of which I feel the metallurgists should change. One is the term "junkman." The trade is trying to clean house and is employing metallurgists today. The metallurgist is coming to the fore in the secondary metal field as well as in the secondary smelters. I prefer the term "waste-material dealers." In a way, even it is not true. The term "waste" itself is a misnomer if what we are talking about means anything, but "reclaimable material" sounds a little awkward, and we are still searching for a better term. I do not like the word "junkman" because very few of the men here today deal with the junkman. If anybody, he is the little chap who collects the city waste.

It is surprising to note the type of men who are getting into the waste-material business today. The large universities and colleges that are represented by the younger generation and the efforts of the older generation, partly through the trends of our minds today, are forcing a change, but the business is getting on to a sound basis, and the waste-material dealers have found that they had to come to the metallurgist. Therefore, the metallurgist should help them as much as he can.

The other term to which I object is "metallics." We find it very confusing. I presume it is intended to mean a metallic button obtained by a fire assay, or something like that, but speaking from the chemical as well as the metallurgical viewpoint, the term "metallic" should hardly be used by the metallurgist, because it means a screening product of metallic character and it is a source of confusion when it comes to the valuation of these materials if used too generally.

H. M. ST. JOHN (written discussion).—Mr. Graham's objection to the use of the term "secondary" in describing scrap materials seems to me not well founded. Unless we are to introduce the word "tertiary" in an already complicated terminology it seems most logical to designate virgin metals as "primary" and all metals that have been or are to be reclaimed for re-use as "secondary."

The secondary refiner performs a necessary function in collecting, classifying and refining miscellaneous non-ferrous metals so that they are once more fit for foundry use in making castings. No one conversant with the industry would seriously suggest that this work could be performed as effectively and economically by the foundry. A more careful reading of the paper would acquaint Mr. Graham with the fact that the writer does not recommend the purchase or use of miscellaneous scrap by the foundry.

The sole question is whether a company that produces in its own operations waste materials not suitable for direct re-use in the foundry can more profitably sell these materials to a secondary smelter or work them up in its own plant for its own use. If it sells them it will buy them back in the form of composition ingot at a price that includes one or two outside profits in addition to transportation costs and handling to and from the plant. If it uses these materials in the manufacture of ingot for its own use these useless costs are eliminated but, to a greater or less extent, it will be necessary to buy outside secondary materials to supplement those originating in the plant itself. Wrought metal scrap of known composition or clean turnings which can be sampled and analyzed readily are most suitable for this purpose. Miscellaneous scrap and metal-bearing wastes are not suitable.

If the waste materials originating in the plant are sufficient in quantity to make up a considerable portion of the metal used in ingot making it is a comparatively simple matter to manufacture a high grade of ingot at a cost substantially less than the market price for such ingot. If nearly all of the material must be purchased from outside sources it becomes more difficult, and may be impossible, for the foundry to produce ingot at a profit. As stated in the paper, clean turnings of known composition, purchased from a known source, may often be used directly in the foundry melt without in any way impairing the quality of the resulting castings. This is obviously more economical than it would be to use these same turnings after they had been melted down into ingot. It should be unnecessary to add that the cost of ingot making by the foundry ought to be determined as carefully and honestly as the cost of any other manufacturing operation.

T. A. WRIGHT.—I am convinced that a number of ingot makers—secondary metal producers—are more particular about what goes into their ingot, judging from the amounts and types of some of the metal which they themselves scrap and sell to copper refineries, than possibly the metallurgical trade understands. In these days of high cost and low margin, they have found it necessary to be very particular; they often do scrap what may seem to be ordinary, clean material, and it is to be regretted that it should have to go through a refining operation.

Oxides in Brass

By O. W. Ellis,* Toronto, Canada

In view of the extensive use of the brasses and bronzes in engineering practice it is indeed surprising that so little scientific work has been done on the oxides in these alloys. Recognition of the ill effects of these compounds is universally accorded, both in foundry procedure and in such specifications as cover the melting of these useful mixtures. In the latter, limits, for example, are placed on the proportions of scrap metal in the charge, and clauses governing the use of fluxes are included, the addition of fluxes to the charge being made with the object of avoiding oxidation during the process of melting and of subducing and separating non-metallic matter from the melt.[1]

In the manufacture of brass it occasionally, though rarely, occurs that the virgin metals, copper and zinc, alone are used. In the event of virgin metals being employed, that of the higher melting point is always melted first. If it is melted under suitable conditions, little or no oxidation will occur. Whether oxidation has occurred or not, however, can best be determined by microscopic examination of a sample taken from the melt.

Avoidance of Oxidation in Furnace Practice

When melting virgin copper in crucible practice, the avoidance of oxidation is not difficult, nor is it hard to forestall trouble in the electric furnace. In gas-fired furnaces of the barrel type, however, the avoidance of oxidation is almost impossible, no matter what the condition of the flame, the flux employed, or the amount of charcoal included in the charge. Copper melted in furnaces of this type is almost invariably so highly oxidized as to require very considerable additions of such deoxidizers as, for example, silicon copper to render it free from cuprous oxide. As a result, the castings produced are decidedly inferior, on account of the large amount of silica which is engendered in the metal as a result of the reaction,

$$Cu_2O + Si = SiO_2 + 2Cu.$$
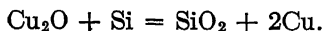
The deoxidation of such oxidized copper could, of course, be effected by means of zinc with, however, even more disastrous results.

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[1] R. Genders and M. A. Haughton: The Use of Fluxes in Brass Melting. *Trans. Faraday Soc.* (1924) **20,** 124.

On the other hand, in oil-fired furnaces of the barrel type the flame may be so adjusted as to ensure the almost complete deoxidation of oxidized copper, provided some charcoal is included in the charge.[2] Hence, in such practice the oxidation of brass within the furnace can be almost wholly avoided, even though the affinity of zinc for oxygen is greater than that of copper for this element. One or two observations of the oxide content of brass melted in an oil-fired Schwartz furnace have made it clear that little, if any, change in oxide content occurs during periods of from 10 min. to 2 hr., the brass standing in the molten state under a suitable flux and the flame (when burning) being so adjusted that, other things being equal, no oxidation of virgin copper under a similar flux would occur in the furnace during and subsequent to fusion.

It should be noted that zinc is vaporized under the above conditions and is oxidized at the mouth of the vessel during and after fusion. Some of the zinc oxide is deposited on the lip of the vessel and can be dislodged in such a way as to fall into the vessel and thus contaminate the melt. Ordinarily, however, such contamination is prevented by the supernatant slag, which entraps the oxide and arrests its entry into the melt.

It may also be observed that a far too common practice in charging furnaces of the barrel type is to fill them to the full with scrap and then to pile excess material (brass) above the charging door. However reducing the conditions within the barrel may be during the melting period, those outside the barrel are distinctly oxidizing. As a result wholesale oxidation of the brass occurs within and in the neighborhood of the flame outside the door and relatively large lumps of zinc oxide fall into the furnace to be absorbed and in part retained by the melt,[3] which at this time is insufficiently protected from contamination, owing to the flux still being in a pasty state. Experience shows that brass melted under these conditions, even though the charge contain a high percentage

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[2] O. W. Ellis: Absorbability of Gases in Casting Copper and Effect of Adding Cuprosilicon. *Trans.* A. I. M. E., Inst. Metals Div. (1929) 443.

[3] It is not suggested that the zinc oxide which falls into the furnace to be absorbed and in part retained by the melt remains in the melt in its original massive state. A certain proportion of this zinc oxide enters into solution in the melt. A certain proportion is broken up into fine particles. It is these fine particles, which are extremely difficult to separate from the melt under the action of gravity and which, therefore, cannot be removed from the melt even by skimming, to which the author is referring throughout this paper. It is, of course, difficult to state definitely that the particles under discussion in this paper are particles of zinc oxide. In view of the fact, however, that they have the same general shape and appearance as certain non-metallic particles which have been described both by Genders and Haughton (*loc. cit.*) and by Comstock,[4] who refer to them as zinc oxide, the author has assumed that they are none other than particles of this compound.

[4] G. F. Comstock: Non-metallic Inclusions in Bronze and Brass. *Trans.* A. I. M. E. (1919) **60**, 386.

of virgin metal, will be useless for the manufacture of high-grade sand castings.

PROCEDURE OF EXPERIMENTS

In the experiments about to be described brass was melted in an oil-fired furnace of the barrel type, care being taken to keep the flame conditions and the charging conditions as constant as possible throughout the entire series. Such objectionable practices as have just been described were carefully avoided, and the condition of the flame was such that oxidized copper, similarly charged and similarly fluxed, would have been largely, if not completely, freed from cuprous oxide during and after fusion. In brief, all factors that could be controlled were kept as fully in hand as possible with the exception of the nature of the charge (proportions of flux, scrap, etc.), it being the author's idea to determine what effect the nature of the charge had upon the amount of oxide contained in the solid brass. The brass investigated was made to the following specification:

	PER CENT.
Copper	Not less than 84
Zinc	4 to 10
Tin	2½ to 6
Lead	1 to 4
Other metals	Not more than 0.2

All the heats were made in a 42-in. oil-fired Schwartz furnace. The earlier heats were melted under the supervision of the author and W. J. Laird, metallurgist of the Linhart foundry of the Westinghouse Electric & Manufacturing Co., East Pittsburgh, Pa., the latter heats under the direction of Mr. Laird alone. The regular routine of foundry practice was interfered with as little as possible. Complete data of each heat regarding the proportions of scrap and ingot, the character of the scrap, the amount of flux, the time occupied in melting, the time the charge was in the furnace between pourings, etc., are given in Table 1.

It will be gathered from Table 1 that after the charge had been melted and prepared for pouring, two test samples were cast, one in a chill mold (marked C), the other in sand. The chill mold was open at the top and was approximately 6 in. long by 1 in. wide by 1½ in. deep. The sand castings were of the general dimensions shown in Fig. 1.

RESULTS OF TESTS

From both the chill and the sand castings tensile test pieces were machined, the tests on these pieces being conducted under the supervision of Messrs. Eakin and McGregor, of the Materials and Processes Department of the Westinghouse Electric & Manufacturing Co. The results of these tests are shown in Tables 2 and 3.

TABLE 1.—*Data of Experimental Heats*

HEAT 1, TESTS 1 AND 2, APRIL 16, 1928

Charge   —750 lb. clean gates and risers and mechanically defective castings.
Flux   —8¼ lb. soda ash added with charge.
Charging —At 7:55 a. m.   All scrap within furnace, door closed on finishing charging.
Skimming—At 8:55 a. m.   Slag viscous.
Alloying —30 lb. Zn added after skimming.
Pouring —First ladle poured at 9:20 a. m.
           Temperature at furnace, 1300° C.
           Test No. 1C poured at 1300° C.
           Test No. 1 poured at 1100° C.

           Third ladle poured at 9:37 a. m.
           Temperature at furnace, 1220° C.
           Test No. 2C poured at 1220° C.
           Test No. 2 poured at 1180° C.

HEAT 2, TESTS 3 AND 4, APRIL 16, 1928

Charge   —750 lb. scrap (splashings, bin-cleanings, etc., charge of worst material on
           hand).
Flux   —None.
Charging —Completed and door closed at 12:15 p. m.
Skimming—At 12:57 p. m.   Slag dry and powdery.
Alloying —35 lb. Zn added after skimming.
Pouring —First ladle poured at 1:35 p. m.
           Temperature at furnace, 1300° C.
           Test No. 3C poured at 1300° C.
           Test No. 3 poured at 1200° C.

           Third ladle poured at 1:54 p. m.
           Temperature at furnace, 1280° C.
           Test No. 4C poured at 1280° C.
           Test No. 4 poured at 1190° C.

HEAT 3, TESTS 5 AND 6, APRIL 27, 1928

Charge   —600 lb. gates and risers.
Flux   —None.
Charging —All scrap within furnace and door closed at 12:30 p. m.
Skimming—Skimmed at 1:45 p. m.
Alloying —30 lb. Zn added after skimming.
Pouring —First ladle poured at 2:00 p. m.
           Temperature at furnace, 1300° C.
           Test No. 5C poured at 1300° C.
           Test No. 5 poured at 1240° C.

           Third ladle poured at 2:16 p. m.
           Temperature at furnace, 1220° C.
           Test No. 6C poured at 1220° C.
           Test No. 6 poured at 1210° C.

TABLE 1.—(*Continued*)

HEAT 4, TESTS 7 AND 8, APRIL 28, 1928

Charge   —600 lb. clean gates and risers.
Flux   —8½ lb. soda ash added with charge.
Charging —At 7:45 a. m.
Skimming—At 8:40 a. m.
Alloying —24 lb. Zn added after skimming.
Pouring   —First ladle poured at 9:20 a. m.
             Temperature at furnace, 1300° C.
             Test No. 7C poured at 1290° C.
             Test No. 7 poured at 1260° C.

             Second ladle poured at 9:35 a. m.
             Temperature at furnace, 1300° C.
             Test No. 8C poured at 1300° C.
             Test No. 8 poured at 1260° C.

HEAT 5, TESTS 9 AND 10, MAY 7, 1928

Charge   —600 lb. clean gates and risers.
Flux   —8 lb. soda ash added with charge.
Charging —At 1:25 p. m.
Skimming—At 2:20 p. m.
Poling   —Poled for 2½ min.
Alloying —24 lb. Zn added after poling.
Pouring   —First ladle at 2:45 p. m.
             Temperature at furnace, 1290° C.
             Test No. 9C poured at 1290° C.
             Test No. 9 poured at 1230° C.

             (After pouring one ladle, gas off from 3 to 3:45 p. m.)
             Second ladle at 4:10 p. m.
             Temperature at furnace, 1250° C.
             Test No. 10C poured at 1250° C.
             Test No. 10 poured at 1230° C.

HEAT 6, TESTS 11 AND 12, MAY 8, 1928

Charge   —710 lb. ingot, heat No. 2944. Analysis: Cu, 82.00; Zn, 12.26; Sn, 2.88;
             Pb, 2.71; Fe, 0.15.
Flux   —None.
Charging —At 7:15 a. m. (oil off, 8:15 a. m. to slow down charge; oil on, 8:40 a. m.).
Skimming—At 9:10 a. m. Slag dry and powdery.
Alloying —No Zn addition to charge.
Pouring   —First ladle poured at 9:40 a. m.
             Temperature at furnace, 1300° C.
             Test No. 11C poured at 1300° C.
             Test No. 11 poured at 1270° C.

             Second ladle poured at 9:55 a. m.
             Temperature at furnace, 1300° C.
             Test No. 12C poured at 1300° C.
             TestNo. 12 poured at 1270° C.

TABLE 1.—*(Continued)*

HEAT 7, TESTS 13 AND 14, MAY 8, 1928

Charge —620 lb. ingot, heat 2944. Analysis: Cu, 82.00; Zn, 12.26; Sn, 2.88; Pb, 2.71; Fe, 0.15.
Flux —8 lb. soda ash added with charge.
Charging —At 10:45 a. m.
Skimming—At 12:10 p. m. Slag viscous.
Alloying —No Zn added to charge.
Pouring —First ladle poured at 12:35 p. m.
Temperature at furnace, 1300° C.
Test No. 13C poured at 1300° C.
Test No. 13 poured at 1270° C.

Second ladle poured at 12:50 p. m.
· Temperature at furnace, 1300° C.
Test No. 14C poured at 1300° C.
Test No. 14 poured at 1270° C.

HEAT 8, TESTS 15 AND 16, MAY 9, 1928

Charge —900 lb. ingot, heat 2944. Analysis: Cu, 82.00; Zn, 12.26; Sn, 2.88; Pb, 2.71; Fe, 0.15.
Flux —None.
Charging —At 7:40 a. m
Skimming—At 8:25 a. m. Slag dry and powdery.
Alloying —No Zn added to charge.
Pouring —First ladle poured at 9:25 a. m.
Temperature at furnace, 1300° C.
Test No. 15C poured at 1300° C.
Test No. 15 poured at 1260° C.

Third ladle poured at 9:35 a. m.
Temperature at furnace, 1300° C.
Test No. 16C poured at 1300° C.
Test No. 16 poured at 1260° C.

HEAT 9, TESTS 17 AND 18, MAY 10, 1928

Charge —710 lb. ingot, heat 2944. Analysis: Cu, 82.00; Zn, 12.26; Sn, 2.88; Pb, 2.71; Fe, 0.15.
Flux —8½ lb. soda ash added with charge.
Charging —Finished at 7:30 a. m.
Skimming—At 8:25 a. m.
Alloying —No Zn added to charge.
Pouring —First ladle poured at 9:05 a. m.
Temperature at furnace, 1270° C.
Test No. 17C poured at 1270° C.
Test No. 17 poured at 1250° C.

Second ladle poured at 9:14 a. m.
Temperature at furnace, 1270° C.
Test No. 18C poured at 1270° C.
Test No. 18 poured at 1240° C.

TABLE 1 *(Continued)*

HEAT 10, TESTS 19 AND 20, MAY 11, 1928

Charge   —800 lb. gates and risers.
Flux   —9 lb. soda ash added with charge.
Charging —At 7:20 a. m.
Skimming—At 8:25 a. m.
Poling   —Poled 2½ min.
Alloying —32 lb. Zn added after poling, 8:35 a. m.
Pouring —First ladle poured at 9:05 a. m.
              Temperature at furnace, 1300° C.
              Test No. 19C poured at 1300° C.
              Test No. 19 poured at 1270° C.

              Second ladle poured at 9:12 a. m.
              Temperature at furnace, 1290° C.
              Test No. 20C poured at 1290° C.
              Test No. 20 poured at 1260° C.

HEAT 11, TESTS 21 AND 22, MAY 15, 1928

Charge   —730 lb. gates and risers.
Flux   —None.
Charging —At 7:35 a. m.
Skimming—At 8:40 a. m.   Slag dry and powdery.
Alloying —30 lb. Zn added after skimming; 4.9 lb. of 15 per cent. phosphor-copper
              added after Zn addition.
Pouring —First ladle poured at 9:25 a. m.
              Temperature at furnace, 1300° C.
              Test No. 21C poured at 1300° C.
              Test No. 21 poured at 1260° C.

              Second ladle poured at 9:35 a. m.
              Temperature at furnace, 1310° C.
              Test No. 22C poured at 1310° C.
              Test No. 22 poured at 1270° C.

Chemical analyses, the results of which are shown in Table 4, were made on all the samples.

In Tables 2 and 3 the samples are arranged in order of increasing copper content, and details are also given of the number of oxide particles per cubic centimeter of sample and of the average area in square centimeters of the oxide particles observed and measured in each sample. In determining the number of oxide particles per cubic centimeter of sample, a count was made of the number of oxide particles in a strip 1 cm. in length, the width of the strip being the diameter of the field seen through a Zeiss microscope equipped with a 4-mm. objective and a 10-X eyepiece. The average area of the particles was determined planimetrically, cross-sections of the particles having first been drawn on tracing paper at a magnification of 1000 dia. In this connection the author desires to express his appreciation of the help afforded him by

Miss M. Ferguson, of the Research Department of the Westinghouse Electric & Manufacturing Co., in the preparation of the microsamples and in the planimetric measurement of the oxide particles.
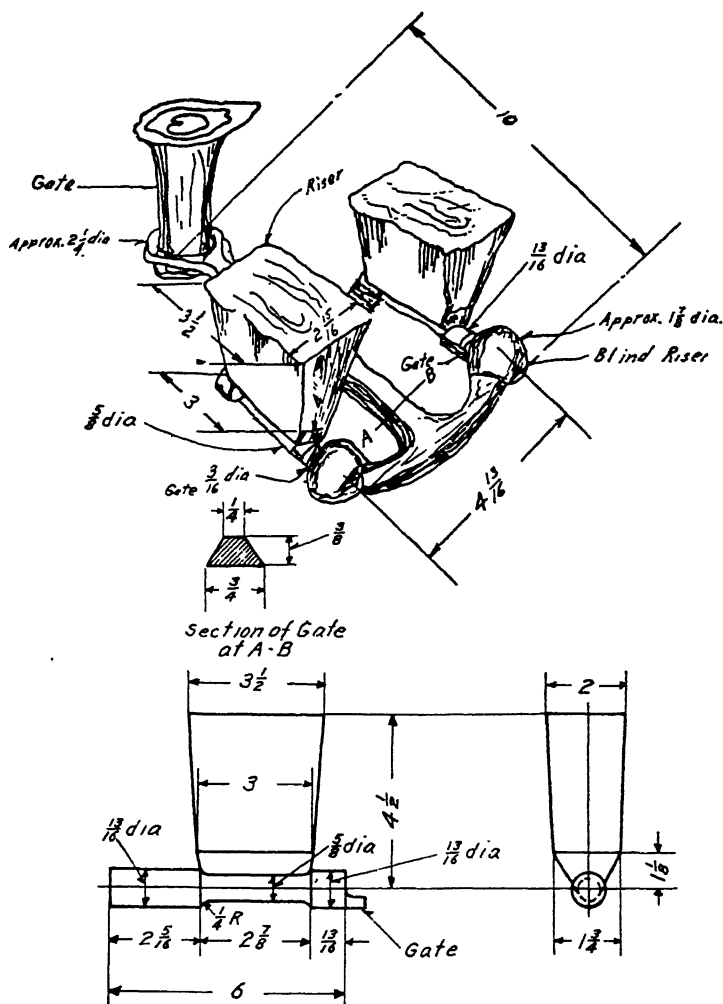
FIG. 1.—SAND CASTINGS, SHOWING DIMENSIONS.

The oxide particles were similar in appearance to those which have been described by Genders and Haughton[5] and by Comstock.[6] Photomicrographs of such particles at magnification of 1000 dia. are shown in Fig. 2. It may be noted that in polishing the samples for microscopic

[5] R. Genders and M. A. Haughton: *Loc. cit.*
[6] G. F. Comstock: *Loc. cit.*

TABLE 2.—*Results of Tests on Chill Castings*
Arranged in Order of Increasing Copper Content

No.	Cu, Per Cent.	Zn, Per Cent	Sn, Per Cent.	Pb, Per Cent.	Number of Oxide Particles per Cu. Cm.	Area of Oxide Particles (Sq. Cm.)	Tensile Strength	Elongation, Per Cent.	Reduction of Area, Per Cent.
1	83.34	10 66	3.28	2.62	790,000	2.45 by 10^-7	20,500	12 0	14 7
4	83.42	10.79	3.15	2.52	1,050,000	2 58 by 10^-7	36,625	33.3	30 7
19	83 86	10.19	3.10	2.74	1,050,000	2 32 by 10^-7	25,950	17.2	53.7
3	84 08	10.22	3 10	2.49	1,450,000	4 71 by 10^-7	32,875	22.4	27.4
2	84 14	9.87	3.28	2.62	1,155,000	2 65 by 10^-7	34,000	27 0	24.0
10	84 24	9 85	3 27	2.54	675,000	2 77 by 10^-7	38,875	38 0	34 6
20	84 40	9 63	3.12	2.78	483,000	1 61 by 10^-7	31,750	28 8	37.8
13	84.88	8.96	3.18	2.86	944,000	1.81 by 10^-7	28,500	35 2	37.5
14	85 13	8 59	3 13	2.86	455,000	1 61 by 10^-7	34,750	30.8	32.7
9	85 48	8.66	3 23	2.53	1,285,000	1 81 by 10^-7	31,000	20.0	27 8
7	85.70	8.58	3 20	2.40	483,000	1 61 by 10^-7	34,125	29 3	32.0
17	86.10	7.82	3 06	2.90	515,000	2 38 by 10^-7	32,300	28 7	29 1
8	86 24	8.08	3 17	2.43	547,000	3 10 by 10^-7	37,075	37 3	34 0
5	86 50	7.66	3 39	2.35	675,000	1.61 by 10^-7	33,750	23 0	26.7
18	86 68	7.30	3.07	2.85	388,000	3.80 by 10^-7	31,550	28.8	35.0
6	86 70	7.28	3 39	2.52	727,000	1 94 by 10^-7	21,625	8 7	11.0
15	87.02	7.04	3 04	2.78	515,000	2 19 by 10^-7	32,250	24.0	26.4
11	87 06	6.79	3.18	2.87	626,000	4 13 by 10^-7	31,750	23 0	21 2
21	87 22	6.83	3 15	2.71	630,000	1.74 by 10^-7	35,625	32 4	34 6
16	87 40	6.46	3.18	2.86	1,155,000	3.61 by 10^-7	26,750	14 5	25 0
12	87.50	5.67	3.21	3.10	1,910,000	2 52 by 10^-7	36,500	22.5	31.7
22	87.56	6.48	3.16	2.71	1,047,000	3 29 by 10^-7	33,250	24 4	36 9
				Average	843,000	2.56 by 10^-7	31,900	25.5	30 2

TABLE 3.—*Results of Tests on Sand Castings*
Arranged in Order of Increasing Copper Content

No.	Cu, Per Cent.	Zn, Per Cent.	Sn, Per Cent.	Pb, Per Cent.	Number of Oxide Particles per Cu Cm	Area of Oxide Particles (Sq. Cm.)	Tensile Strength	Elongation, Per Cent.	Reduction of Area, Per Cent.
3	82.88	11.70	3.01	2.31	257,000	6 45 by 10^-7	29,500	24.8	26.5
1	83 44	10.79	3 26	2.40	200,000	7 53 by 10^-7	34,250	29.7	35.9
19	83.85	10.05	3.15	2.84	127,000	6.45 by 10^-7	30,125	24.6	31.5
10	84.06	9.83	3 33	2.67	95,000	8 58 by 10^-7	35,250	35.3	35 9
4	84 26	10.04	3 23	2.88	350,000	6 33 by 10^-7	32,060	24.9	29.0
20	84.88	9.15	3.10	2.76	142,000	9 87 by 10^-7	28,010	22.4	31.9
13	85 12	8.70	3 18	2.87	95,000	8 97 by 10^-7	29,375*	21.7*	29.1*
14	85.52	8.72	3.10	2.83	71,000	7.42 by 10^-7	27,250	20.2	28.4
9	85 52	8.28	3.38	2.70	158,000	9.66 by 10^-7	36,750	28.0	28.1
7	85.76	8.45	3 29	2.40	187,000	6 64 by 10^-7	34,000	31.0	30.4
17	86 00	7.91	3.12	2.85	71,000	10 78 by 10^-7	28,130	21.5	28.3
5	86.42	7.70	3.43	2.35	214,000	9 29 by 10^-7	27,380	17.4	27 3
18	86 59	7.12	3.15	3.01	155,000	7 22 by 10^-7	26,400	22.7	27.0
8	86 64	7.64	3.19	2.43	184,000	7.22 by 10^-7	30,750	22.7	26.3
6	87.10	6.92	3.42	2.46	176,000	7.03 by 10^-7	25,500	17.1	24.5
11	87 10	6.75	3.16	2.87	257,000	6.25 by 10^-7	31,060	23.0	26 1
15	87.19	6.63	3.19	2.88	105,000	6.45 by 10^-7	29,430*	19.5*	21.2*
21	87.20	6.61	3.28	2.79	249,000	2.45 by 10^-7	29,250	20.7	30.0
16	87 99	5.95	3.12	2.83	179,000	10.20 by 10^-7	26,280	20.5	30.7
22	88.04	5.97	3.22	2.69	318,000	4 32 by 10^-7	27,280	20.6	27.7
12	88.06	5.75	3.17	.219	200,000	4.19 by 10^-7	33,250	24.4	36 9
				Average	181,000	7.30 by 10^-7	30,000	22.4	29.2

* One tensile test only.

No observation was made on the sand casting from heat No. 2, this having been lost in transit from the foundry to the laboratory.

<div align="center">TABLE 4.—Chemical Analyses of Samples</div>

Mark	Cu, Per Cent.	Zn, Per Cent.	Sn, Per Cent	Pb, Per Cent.	Fe, Per Cent.
1 1C	83.44 83.34	10.79 10.66	3 26 3.28	2.40 2.62	0.11 0.10
2 2C	84.34 84.14	9 79 9.87	3.26 3.28	2 49 2 62	0.12 0.10
3 3C	82.88 84.08	11.70 10.22	3.01 3.10	2 31 2.49	0.10 0.11
4 4C	84.26 83.42	10 04 10.79	3.23 3.15	2.38 2.52	0.09 0.12
5 5C	86.42 86.50	7 70 7.66	3.43 3.39	2.35 2.35	0.10 0.10
6 6C	87.10 86 70	6 92 7.28	3.42 3.39	2.46 2.52	0.10 0.11
7 7C	85.76 85.70	8.45 8 58	3.29 3.20	2.40 2.40	0.10 0.12
8 8C	86.64 86.24	7.64 8.08	3.19 3.17	2.43 2.43	0.10 0.12
9 9C	85.52 85.48	8 28 8 66	3 38 3 23	2.70 2.53	0.12 9.10
10 10C	84.06 84.24	9 83 9.85	3 33 3.27	2.67 2.54	0.11 0.10
11 11C	87.10 87.06	6.75 6.79	3.16 3.18	2.87 2.87	0.12 0.10
12 12C	88.06 87.50	5.75 5.67	3.17 3.21	2.19 3.10	0.12 0.12
13 13C	85.12 84.88	8 70 8.96	3.18 3 18	2.87 2.86	0.13 0.12
14 14C	85.52 85.13	8.72 8.59	3 10 3.13	2.83 2.86	0.12 0.12
15 15C	87.19 87.02	6.63 7.04	3.19 3.04	2.88 2.78	0.11 0.12
16 16C	87.99 87.40	5.95 6.46	3.12 3.18	2.83 2.86	0.11 0.10
17 17C	86.00 86.10	7.91 7.82	3.12 3.06	2.85 2.90	0.12 0.12
18 18C	86.59 86.68	7.12 7.30	3 15 3 07	3.01 2.85	0.10 0.10
19 19C	83.85 83.86	10.05 10.19	3.15 3 10	2.84 2.74	0 11 0.11
20 20C	84.88 84.40	9.15 9.63	3 10 3.12	2 76 2.78	0 11 0.11
21 21C	87.20 87.22	6.61 6.83	3.28 3.15	2.79 2.71	0.12 0.09
22 22C	88.04 87.56	5.97 6.48	3 22 3.16	2.69 2.71	0.08 0 09

examination portions of the particles were occasionally removed from the matrix, showing clearly that the oxide is relatively brittle and friable.

<div align="center">EFFECT OF VARIATION IN ALLOY COMPOSITION</div>

It will be noted that few of the samples referred to in Tables 2 and 3 fall outside the specification limits referred to above, but that a wide

variation exists in both copper and zinc. These variations in zinc and copper content, however, do not appear to have had any effect upon the mechanical properties of the samples. And, it may here be noted, neither is there any noteworthy correlation between the number of oxide particles per cubic centimeter and the tensile strength of the samples (the correlation between these factors in the case of the sand castings, for example, is only 0.0506—practically nil). It is clear that other factors enter into the field, which are of more importance in this connection than are those referred to above. That variations in the composition of this alloy within the limits referred to in the specification are not without effect on its mechanical properties is clearly shown in appendix A of this paper.

FIG. 2.—OXIDE PARTICLES IN BRASS. × 1000.
Reduced ⅓ in size. Original magnification given.

OXIDE IN CHILL VS. SAND-CAST SAMPLES

The outstanding items of interest in Tables 2 and 3 are the differences shown to exist between the numbers and areas of the particles of oxide in the chill and sand-cast samples, respectively. It should be noted that zinc oxide only was observed in all cases, with the possible exception of the samples taken from the alloy which had been treated with phosphor copper (tests 21 and 22). In the case of these samples it appeared that the particles, which were of the general form characteristic of zinc oxide, were slightly darker in color than those observed in the other samples. Further investigation is required in this connection.

That the number of oxide particles per unit volume in chill castings is ordinarily greater than in sand castings has been noted by Comstock[7]

[7] G. F. Comstock: *Loc. cit.*

who does not, however, call attention to the significance of this fact. Surely, the very definite differences in the size and number of particles observed can be accounted for only on the assumption that zinc oxide is soluble in the liquid alloy and that its state of division in the solid alloy is determined in the main by the rate of cooling of the alloy, prior to and during its solidification.

No attempt has been made to estimate in every case the average *volumes* of the oxide particles in the chill and sand castings, respectively, but a comparison of the approximate total volumes of oxide per cubic centimeter of metal in the chill and sand castings from the melts 9 and 14 (which were chosen at random for this purpose) has been made with the results given in Table 5.

TABLE 5.—*Approximate Total Volumes Oxide of Metal in Castings*

Melt 9

	Sand Cast	Chill Cast
Average volume of particles........	36 by 10^{-12} cu. cm.	4.0 by 10^{-12} cu. cm.
Number of particles per cu. cm.....	1.58 by 10^4	1.29 by 10^6
Total oxide per cu. cm. of metal....	56.8 by 10^{-7} cu. cm.	51.4 by 10^{-7} cu. cm.

Melt 14

	Sand Cast	Chill Cast
Average volume of particles........	24 by 10^{-12} cu. cm.	2 4 by 10^{-12} cu. cm.
Number of particles per cu. cm.....	7.1 by 10^4	4 6 by 10^5
Total oxide per cu. cm. of metal....	16.8 by 10^{-7} cu. cm.	10.8 by 10^{-7} cu. cm.

It will be seen that the volume of oxide per cubic centimeter of metal in the two types of casting made from the same melt are very nearly the same. This is as might be expected if it is assumed that the solubility of zinc oxide in the solid alloy is practically nil. A description of the method adopted to determine the volumes of these particles is given in Appendix B.

Nature of Charge and Oxide Count

One of the most important points elicited by this investigation is the fact that a very close connection exists between the oxide count and the character of the charge. This is brought out very clearly in Tables 6 and 7, which themselves are based on Tables 1, 2 and 3.

In Table 6 the relation between the nature of the charge and the average number of oxide particles per cubic centimeter of sample (chill and sand) is shown, together with the average areas of the oxide particles in each case. The groups are arranged in descending order of contamina-

tion. As might be expected, the material resulting from the fusion of a charge consisting entirely of low-grade scrap and including no flux contains by far the greatest amount of oxide, while that resulting from the melting of a charge consisting of ingot and flux is relatively free from inclusions of oxide.

TABLE 6.—*Contamination of Charge*

Character of Charge	Particles per Cu. Cm.			Area of Oxide Particles (Sq. Cm.)		
	Chill	Sand	Mean	Chill $\times 10^{-7}$	Sand $\times 10^{-7}$	Mean $\times 10^{-7}$
Scrap, 100 per cent.; *no soda* ash....................	1,250,000	314,000	782,000	6.39	3.65	5.02
Gates and risers; *no soda* ash; treated with 15 per cent. phosphor-copper ...	839,000	284,000	561,000	3.39	2 52	2.95
Ingot, 100 per cent.; *no soda* ash....................	810,000	185,000	498,000	6.77	3.11	4.94
Gates and risers, soda ash...	743,000	178,000	460,000	7.99	2.45	5.22
Gates and risers; *no soda* ash.................. .	701,000	185,000	448,000	8.16	1.78	4.97
Gates and risers, soda ash, poled....................	623,000	131,000	377,000	8.64	2.13	5.38
Ingot, 100 per cent.; soda ash......	576,000	98,000	337,000	8.59	2.40	5 49

In so far as the areas of the oxide particles are concerned, it appears, as might be expected, that they are but slightly affected by the nature of the change. They tend to vary inversely as the number of particles per cubic centimeter of sample, but this tendency may be apparent rather than real. In this connection, there are certain discrepancies, which cannot be explained. It should be noted that the value quoted for this factor in column 5 of Table 6 in the case of the chill castings made from the charge treated with phosphor-copper was both checked and rechecked. The discrepancies have apparently been occasioned by the presence of phosphorus in the melt—as has been noted above, there appeared to be some difference in the color of the oxide in the samples which had been treated with phosphor-copper. Again it may be suggested that further work is required in this connection.

EFFECT OF RETAINING CHARGE IN FURNACE

In Table 7 the attempt has been made to demonstrate the effect of retaining the melt in the furnace subsequent to the first pouring. In column 3 of this table the numbers of particles per cubic centimeter of the chill samples first poured from the furnace are noted, while in column 5 are given the numbers of particles per cubic centimeter of the

chill samples subsequently poured from the furnace, *i. e.*, after times varying from 7 to 19 min., if one exceptional case (in which the time between pourings was 125 min.) is omitted. In columns 6 and 9 the same values applying to the sand castings are given.

Certain important facts seem to be brought out in this table.

TABLE 7.—*Effect of Flux and Standing on Oxide Content of Brass*

Nature of Charge		Chill Castings			Sand Castings		
Alloy	Flux	Number of Particles per Cu. Cm. (First Pour)	Time of Standing between Pours, Min.	Number of Particles per Cu. Cm. (Second Pour)	Number of Particles per Cu. Cm. (First Pour)	Time of Standing between Pours, Min.	Number of Particles per Cu. Cm. (Second Pour)
All scrap	None	1,450,000	19	1,050,000	257,000	19	350,000
Gates, risers and defective castings	None	675,000	16	727,000	214,000	16	176,000
All ingot	None	626,000	15	1,910,000	257,000	15	200,000
		515,000	10	1,155,000	105,000	10	179,000
Gates, risers and defective castings	No soda ash, phosphor-copper	630,000	10	1,047,000	249,000	10	318,000
Gates, risers and defective castings	Soda ash	790,000	17	1,155,000	200,000	17	N.O.
		483,000	15	547,000	187,000	15	184,000
All ingot	Soda ash	944,000	15	455,000	95,000	15	71,000
		515,000	9	388,000	71,000	9	155,000
Gates, risers and defective castings.	Soda ash, poled	1,285,000	125	675,000	158,000	125	95,000
		1,050,000	7	483,000	127,000	7	142,000

In the first place it appears as though the retention of the charge in the furnace between the first and the second pours *in the absence of flux* tends to increase its content of oxide. In three out of four instances of charges melted without flux an increase of oxide is noted in the chill castings, whose "oxide counts," be it observed, appear to be more reliable as an indication of oxide content on account of the relative uniformity of the particle size in such castings. If to these cases be added that of the charge treated with phosphor-copper, still further support for the foregoing impression is obtained.

In the second place it appears as though *the presence of a flux* tends to retain the oxide content of the melt unchanged during the period of waiting between pours. In the case of certain charges, notably those composed of gates and risers, the oxide content rose during the waiting period. On the other hand, the "oxide count" fell during the waiting period in the case of melts made from all-ingot charges.

Finally, it seems evident that *poling* has a decidedly beneficial effect upon charges to which flux has been added. In both cases where charges so treated were examined, a decided improvement appeared to have occurred during the waiting period.

CONTROL BY "OXIDE COUNT"

There is no question that much further work must be done before a definitive statement of the effects of charge, composition, flux, etc., on the "oxide count" of brass can be made. However, it does appear from the author's preliminary investigations in this field that what he has termed the "oxide count" might be used with good effect in the control of foundry practice in certain cases, since so close a relationship appears to exist between the number of oxide particles per cubic centimeter of sample and the character and treatment of the charge. It is quite clear that the conditions both of taking and making test samples would need to be exactly stated in view of the powerful effect of cooling rates upon the "oxide count." However, in the hands of persons sincerely concerned in the improvement of their product, this method of control appears to present quite interesting possibilities and to merit further investigation and, possibly, standardization as a test in the foundry industry.

ACKNOWLEDGMENT

The writer desires to thank the Westinghouse Electric & Manufacturing Co. for permission to publish the results referred to in this paper, the work having been done while the writer was in its employ.

APPENDIX A

THE EFFECT OF COMPOSITION ON THE PROPERTIES OF A COMPLEX BRASS

In order to determine whether variations in the composition of the brass, to whose specification the alloys referred to in the foregoing paper were made, would affect its mechanical properties, two series of alloys were prepared and melted in an induction furnace under standard conditions. A graphite crucible was used and virgin metals were employed. The copper was melted first. The tin and lead were then added. The zinc was added last and carefully stirred in. No flux was used, but, prior to pouring, the melt was carefully skimmed, and during pouring every precaution was taken to prevent access of oxide to the melt. The alloys were prepared in 10-lb. lots and were poured into chill molds. The castings were in the form of plates, $\frac{3}{4}$ in. thick, 3 in. wide and 6 in. long. From these plates two tensile-test samples and one Izod-test piece were cut. The Izod-test pieces were made with three notches, so that the Izod results quoted below represent the average of three tests. No attempt was made to measure the oxide content of these samples.

Table 8 gives the compositions of the first series of alloys tested and the results of the tests. A consideration of this table will show that when both the proportions of tin and lead and the ratio of tin to lead in these alloys are held constant, there is a *tendency* for the strength

of these alloys as measured by the elastic limit, yield point and tensile strength to increase as their content of zinc is raised. At the same time a very definite change in their resistance to impact occurs, the Izod number being lowered as the zinc content rises.

Approximate analyses of the second series of alloys are shown in Table 9, together with the results of the tests carried out on samples cut from the same, the results of which may be stated as follows:

1. In alloys of this type, in which the copper content is retained at 84 per cent., maximum tensile strength apparently occurs when they contain about 10 per cent. of zinc.

TABLE 8.—*First Series of Alloys Tested and Results of Tests*

Copper, Per Cent.	Zinc, Per Cent.	Tin, Per Cent.	Lead, Per Cent.	Ratio, Tin/ Lead	Elastic Limit, Lb. per Sq. In.	Yield Point		Tensile Strength, Lb. per Sq. In.	Elon- gation Per Cent. on 2 In.	Reduc- tion of Area, Per Cent.	Izod Num- ber, Ft. Lb.
						0.2 Per Cent., Lb. per Sq. In.	0.5 Per Cent., Lb. per Sq. In.				
88.4	6.08	2.91	2.68	1 09	7,700	13,800	15,900	32,300	32.5	35.3	18.3
87.4	6.80	3.06	2.60	1.18	7,400	14,400	15,000	40,400	21.4	40 6	16.5
84.6	10.24	2.75	2.59	1.06	7,800	14,800	16,100	40,000	32.4	34.9	14 7
82.5	12.05	3.05	2.66	1.15	11,500	16,800	17,500	41,500	29.9	33.0	12.3

TABLE 9.—*Second Series of Alloys Tested and Results of Tests*

Copper, Per Cent.	Zinc, Per Cent.	Tin, Per Cent.	Lead, Per Cent.	Johnson Elastic Limit No. 1	Yield Point		Tensile Strength No. 1	Elon- gation, Per Cent. on 2 In.	Reduc- tion of Area, Per Cent.	Izod Num- ber Ft. Lb.
					0.2 Per Cent., Lb. per Sq. In.	0.5 Per Cent., Lb. per Sq. In.				
84.0	6.0	6.7	3.3	13,300	18,800	19,200	37,700	10.9	16.2	8.2
84.0	8.0	5.3	2.7	12,600	16,500	18,800	38,400	16.5	21.9	11.5
84.0	10.0	4	2	10,300	14,700	17,600	39,000	23 7	29.0	12 8
84.0	12.0	2.7	1.3	9,500	12,600	12,800	37,700	29 3	40.0	14 5
84 0	6.0	5.0	5.0	11,900	16,500	18,400	34,000	14.4	21.9	12.2
84.0	8.0	4 0	4.0	9,400	15,900	17,000	36,900	26 8	25.9	12.7
84.0	10.0	3 0	3.0	11,000	13,100	15,000	38,900	35.7	38.1	14.0
84.0	12.0	2 0	2.0	9,000	12,500	13,300	36,400	35.3	38.7	16.7

The total changes in tensile strength, however, are so small that it may be illogical to base any opinions on these results. Further, consideration of the effect of zinc content on the elastic limit and yield points of these alloys tends to the view that increase in zinc leads to a fairly uniform *reduction* of strength.

2. For any given content of copper and zinc, the higher the ratio of tin to lead (within the limits of the specification), the stronger the alloy.

3. The higher the content of zinc, the more ductile is the alloy, no matter what the ratio of tin to lead.

4. For any given content of copper and zinc, the higher the ratio of tin to lead (within the limits of the specification), the less ductile the alloy.

It is, of course, fully realized by the author that these results apply strictly only to chill-cast alloys, and that even in the case of chill-cast alloys further work is desirable. If we assume that the conclusions reached above are correct, then it is quite clear in what direction manufacturers of such alloys should proceed if they would improve the quality of their product. Apparently, in foundry practice there are so many other factors entering in, which tend to modify the character of an alloy in the form of sand castings, that the effect of the various elements upon these properties cannot be readily appreciated from an examination of the results of tests made on castings taken in the foundry.

APPENDIX B

DETERMINATION OF VOLUME OF OXIDE PARTICLES

In arriving at the values quoted on page 327 for the average volumes of the oxide particles in the chill and sand castings of melts 9 and 14, respectively, the following procedure was adopted. The sections of the particles, which had been drawn on tracing paper, were carefully enclosed within ellipses which coincided closely in area with the particles themselves. The ratios of the axes of these ellipses were then determined. To the ratio of individual ellipses the symbol α was applied. Then

$$\beta = \frac{4}{3\sqrt{\pi\alpha}}$$

where β is the multiplicand required to obtain the volume of the particles of which the area is already known.

DISCUSSION

O. W. ELLIS.—I wish to make it clear that the paper represents a cooperative effort on the part of a number of people. I wish first to thank Mr. W. J. Laird, of the Linhart foundry of the Westinghouse Electric & Manufacturing Co. At the beginning of the experiments Mr. Laird worked with me in controlling certain heats that are referred to in the paper, and later took over the control of those heats entirely, leaving me free to go ahead with the investigation in the laboratory. Also, I have to thank Messrs. Eakin and McGregor, of the Materials and Processes Department of the company, for arranging for the mechanical tests of the various castings and Miss Mildred Ferguson, of the Research Department, for her assistance in preparing the microsamples and for making many of the planimetric measurements of the oxide particles.

J. C. BRADLEY, Waterbury, Conn.—Did Mr. Ellis determine zinc oxide chemically? I have seen results of using the method of Evans and Richards[8] on brasses.

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[8] B. S. Evans and H. F. Richards: Determination of Zinc Oxide in Brass. *Jnl* Inst. Metals (1926) **35**, 173.

One brass showed 0.0014, another 0.0068 per cent. oxygen; others, intermediate values.

On page 327, Mr. Ellis showed $56.8 \times 10^{-}$ cu. cm. oxide per cu. cm. of one sample. Assuming a specific gravity of 6 for zinc oxide and 9 for brass, this would mean that Mr. Ellis found 0.000075 per cent. oxygen, or $\frac{1}{20}$ or $\frac{1}{60}$ as much as in the brasses tested by the chemical method.

I wonder how the chemical and microscope methods compare as to accuracy.

O. W. ELLIS.—The work that is described in this paper was completed before I had an opportunity to carry out an investigation on the oxides in brass by chemical means. I had not thought of following the line of the German investigators to whose work I think you have referred. What I had thought of trying was to adopt a sort of modified Dickinsen method to dissolve away all the brass and leave the oxide, then to weigh the oxide or to determine by microscopic means the proportion of oxide that was left undissolved after suitable solvents had been discovered for dissolving away the brass.

I am not surprised at the difference between the results that I have obtained by microscopic means and the results that have been obtained by chemical means, knowing very well how difficult it has been found by a number of workers along that line to get even consistent results on one and the same material. I cannot explain why they should have found so much more oxide than I have been able to find.

Distribution of Lead Impurity in a Copper-refining Furnace Bath

By J. Walter Scott* and L. H. DeWald,* Chicago, Ill.

The removal of lead by fire refining methods from copper of electrolytic quality is growing in importance. Particularly is this true of the refining of secondary copper and copper cathodes obtained from electrolytic cells where lead is used as the anode material, as in the electrolysis of ore-leaching solutions and foul electrolyte.

When investigating the removal of small amounts of lead from molten copper in a reverberatory furnace during the refining of secondary copper of otherwise electrolytic copper quality,[1] it was found necessary first to
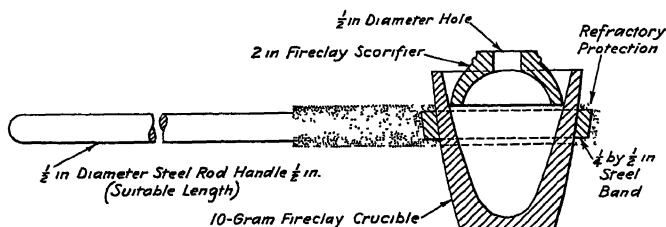
Fig. 1.—Sampling device.

know something about the distribution of the lead throughout the bath. The authors believe that it is not generally known how small amounts of lead as an impurity are distributed in a molten copper bath; that is, whether the lead is concentrated at the bottom or at the top, or whether it occurs more or less uniformly throughout the bath. The data contained in this report may help, therefore, in the development of a satisfactory fire refining method for the removal of this obstinate element from a molten copper bath.

The first step was the development of a method for taking samples from various locations in the bath, at the surface and at various depths. The sampling device used, shown in Fig. 1, consisted of a 10-gram fireclay assay crucible fitted into a ring on the end of a steel rod handle of suitable length. A fireclay scorifier, 2 in. dia., with a ½-in. hole bored in the

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[1] For details of refinery operation, see W. A. Scheuch and J. Walter Scott: Manufacture of Wire Bars from Secondary Copper. Page 289, this volume.

center, was used as a cover. The scorifier was inverted and gently ground into place so that it fitted tightly in the open end of the crucible.

To take a depth sample, the crucible was inverted above the location under which the sample was to be taken. It was then plunged into the copper to the desired depth and held there until all the air was expelled

FURNACE HEAT A
Per Cent

Pb-0.004 / O₂-0.546   Pb-0.004 / O₂-0.516   Pb-0.004 / O₂-0.376   Pb-0.003 / O₂-0.537   Pb-0.009 / O₂-0.411   Pb-0.003 / O₂-0.607

Samples Taken at 3 25 A M

Pb-0.010 / O₂-0.650   Pb-0.005 / O₂-0.695   Pb-0.003 / O₂-0.487   Pb-0.004 / O₂-0.586   Pb-0.003 / O₂-0.687   Pb-0.004 / O₂-0.526

Samples Taken at 4 50 A M

Pb-0.003 / O₂-0.917   Pb-0.003 / O₂-0.767   Pb-0.005 / O₂-0.655   Pb-0.005 / O₂-0.835   Pb-0.004 / O₂-0.776   Pb-0.003 / O₂-1.037

Samples Taken at 5 50 A M

Pb-0.007 / O₂-0.833   Pb-0.003 / O₂-0.847   Pb-0.004 / O₂-0.676   Pb-0.003 / O₂-0.747   Pb-0.003 / O₂-0.637   Pb-0.004 / O₂-0.796

Samples Taken at 6 30 A M

FURNACE HEAT B
Per Cent

Pb-0.015 / O₂-0.755   Pb-0.022 / O₂-0.928   Pb-0.020 / O₂-0.860   Pb-0.021 / O₂-0.829   Pb-0.019 / O₂-0.851   Pb-0.019 / O₂-0.811

Samples Taken at 7 30 P M

Pb-0.013 / O₂-1.157   Pb-0.013 / O₂-1.367   Pb-0.011 / O₂-1.219   Pb-0.010 / O₂-1.160   Pb-0.009 / O₂-1.291   Pb-0.012 / O₂-1.998

Samples Taken at 9 00 P.M.

Pb-0.008 / O₂-1.722   Pb-0.010 / O₂-1.390   Pb-0.006 / O₂-1.684   Pb-0.009 / O₂-1.681   Pb-0.010 / O₂-1.390   Pb-0.010 / O₂-1.690

Samples Taken at 10·30 P M.

Pb-0.006 / O₂-1.634   Pb-0.006 / O₂-1.644   Pb-0.005 / O₂-1.434   Pb-0.007 / O₂-1.663   Pb-0.003 / O₂-1.427   Pb-0.005 / O₂-1.675

Samples Taken at 6 00 A M

FIG. 2.—SECTIONS THROUGH MOLTEN COPPER-REFINING BATHS, SHOWING DISTRIBUTION OF LEAD AND OXYGEN.

from the crucible and the molten copper had replaced it. This time was easily determined, because bubbles ceased to come to the surface and the buoyant effect of air in the crucible was no longer felt on the handle of the sampler. The crucible was then quickly turned upright and brought to the surface. The time actually required to take the sample rarely exceeded 10 seconds.

The same sampling equipment, without the scorifier cover, was used to take a surface sample.

The copper baths sampled were contained in a 45-ton reverberatory furnace and were being refined for wire-bar production. The hearth dimensions of the furnace were approximately 13 ft. 0 in. long by 7 ft. 0 in. wide. Each bath of copper was approximately 2 ft. 0 in. deep at the front and tapered at a more or less uniform rate along the bottom toward the back, where it was only approximately 6 in. deep.

The results of two series of samples taken during the progress of the refining (oxidizing) periods of two separate furnace heats and analyzed for lead[2] and approximate oxygen[2] are shown diagrammatically in Fig. 2 as cross-sections of the bath. The samples were taken on the approximate center line of the length of the furnace as follows: Samples at the front were taken on the surface, halfway down, and on the bottom; samples midway between the front and back were taken on the surface and on the bottom; and a sample at the back was taken on the surface only. For 10 min. before taking the samples the heat was allowed to be quiet; that is, the usual working with rabbles and mixing by blowing with air was stopped.

On the basis of the diagrams, it may be stated that:

1. In general, lead occurs more or less uniformly distributed throughout the bath.

2. As the oxidation progresses there is a slight tendency for the lead to concentrate toward the surface.

3. Initial reduction of lead content is easier when larger amounts of lead are present.

4. As would be expected, the oxygen content increases progressively during the oxidation period and decreases with depth.

In conclusion, it is apparent that efficient fire refining methods using slags for removing small amounts of lead from molten copper in a reverberatory furnace must take into consideration two factors: (1) The lead must be in the oxidized condition so that it may unite with the carrier slag; (2) a high degree of agitation must be effected in order that all particles of copper that contains lead may come in contact with the carrier slag.

DISCUSSION

S. SKOWRONSKI, Perth Amboy, N. J.—The authors are unduly concerned about the possibility that refined copper may contain lead. After melting thousands of tons of copper cathodes from the Southwest, containing 0.02 to 0.03 per cent. of lead, obtained by electrolytic recovery using insoluble lead anodes, it may be stated that the lead in or on the cathodes is completely removed during the usual furnace operations.

Knowing the difficulty of the secondary metal plants in the removal of traces of lead from copper, careful tests were made on full furnace charges (300 tons) and it

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[2] Lead analyses were made by electrolytic method. Oxygen percentages are approximate; they were made by analyzing samples for copper plus silver, adding the percentage of lead content, and calling oxygen the difference between this figure and 100 per cent.

was with considerable relief that it was found that lead was completely removed without any extra furnace treatment.

The ease of removal of the lead is undoubtedly due to the fact that lead on or in the cathodes is present mainly in the form of lead peroxide, which readily slags off.

In view of the many contradictory statements in the literature on the effect of lead in copper, it would be appreciated if the authors would inform us as to what their experience has been regarding the effect of small quantities of lead on copper and what they consider the maximum amount of lead permissible in copper to be drawn into wire or rolled into sheets.

C. T. EDDY, Houghton, Mich. (written discussion).—Though reverberatory refining in the Lake Superior district is not directly concerned with the removal of lead, the author's paper was read with interest. It was, however, not surprising that the lead was found to be rather uniformly distributed throughout the bath. Notwithstanding the partial solubility of lead in copper in the liquid state, small proportions such as were encountered in the two charges investigated by the authors are readily soluble.

Regarding the tendency of lead to concentrate near the surface during rabbling, an examination of the data shows this tendency to manifest itself distinctly in only two or three instances. Only in these cases were the analyses found to differ by amounts essentially different from the variation found between the surface samples themselves. In fact, some of the samples taken from the interior showed lead contents higher than corresponding surface samples. Even PbO, the form in which the lead enters the slag, has a specific gravity between 9.0 to 9.5, depending upon the form of the oxide and, obviously, will not come to the surface unless the lead content is above 25 per cent. This would make apparent the necessity for the high degree of agitation which the authors found to be necessary.

The third conclusion is entirely in accord with the natural chemical phenomena which would be expected to take place under conditions such as those described, and is true not only for lead but for other impurities. It follows also that the lead must be in the oxide form to unite with the slag.

C. S. WITHERELL, New York, N. Y.—I think we should also have from the authors photomicrographs illustrating the effect a small amount of lead has on copper. While it may be true that a few thousandths of a per cent. of lead in copper is not discernable as a recognizable constituent under the microscope, nevertheless, a very small amount may alter the appearance of the copper suboxide. Furthermore, optically determined oxygen in copper means more than oxygen determined by difference, in that it conveys to the metallurgist some idea of the microstructure of the cast copper.

J. W. SCOTT.—The authors agree with Mr. Skowronski that the manner in which lead occurs in the copper affects the ease of its removal by fire-refining methods. Unfortunately, secondary copper refiners frequently encounter lead impurity in the metallic state, in which condition it offers considerable difficulty of removal.

A true maximum amount of lead permissible in copper to be drawn into wire has not been satisfactorily determined for all conditions of processing, so far as the authors know. However, based on the data they have obtained on the subject, they rather arbitrarily consider that copper which is to be processed into fine-sized annealed wire should contain not over 0.005 per cent. lead and also be of proper quality otherwise. Considerable amounts of lead appear to retard the low-temperature annealing of copper and it is important therefore not to mix wire from coppers of high and low lead content within a single annealing furnace charge if uniformly annealed wire is desired. If large-sized hard wire is being produced, the limit of 0.005 per cent. lead apparently may be raised considerably; possibly it may be doubled or even trebled.

Comparison of Copper Wire Bars Cast Vertically and Horizontally

By J. Walter Scott* and L. H. DeWald,* Chicago, Ill.

It is usual practice in the copper industry to use open horizontal molds for casting tough-pitch copper wire bars.[1] A wire bar cast in this manner is partly characterized by heavy wrinkles and a comparatively deep skin of oxide on the top of the bar, corresponding to the open side of the mold. On the theory that the rough, high-oxide surface might have an adverse effect on the rolling and drawing properties of a wire bar and might account for some of the irregularities of mill behavior, several bars which had been planed to remove the wrinkled surface were processed into wire. These bars responded to mill treatment more satisfactorily than did the regular wire bars.

Realizing that machining the surface of one face of each bar would not be commercially feasible, it was decided that casting the metal into a vertical mold and cropping off the pouring end would accomplish approximately the same result. Several wire bars of commercial size (250 lb.) were so cast and processed into wire for comparative test with bars cast in the usual horizontal molds.

It is the purpose of this paper to present the results obtained from this investigation, in which commercial bar sizes and processing technique were used throughout. The results show that in general copper wire bars cast vertically are superior to those cast horizontally.

Experimental Procedure

A horizontally cast bar and a vertically cast bar were obtained from each of several regular reverberatory furnace heats of copper which had been refined and poled to tough-pitch metal in accordance with usual methods.[2] Both bars were cast from the same part of the melt and within five minutes of each other, in order to produce as nearly as possible, in each case, wire bars of identical composition.

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[1] Since this paper was written, it has come to the authors' attention that one of the large American copper refiners is casting tough-pitch copper cake in vertical instead of the usual horizontal molds. It is claimed that the cake cast vertically is a superior product.

[2] For refining details, see W. A. Scheuch and J. Walter Scott: Manufacture of Wire Bars from Secondary Copper. Page 289, this volume.

The horizontal bars were cast by hand, using a bull-ladle, into a one-bar mold made of copper, which weighed approximately 1300 lb. Approximately 15 sec. time was required to cast the 250 lb. of metal.

The vertical bars were cast into a mold of the same type as that used for the horizontal bars, modified so that it could be placed on end to receive the copper. In this way the same ratio of mold to bar weight was maintained for the vertical and horizontal bars. The temperature of the vertical mold previous to casting was approximately 250° F., which is practically the same as the usual horizontal-mold temperature. Each vertical bar was cast as rapidly as possible because quick pouring minimized "cold sets" or metal shots. Approximately 20 sec. time, excluding the time for filling the shrinkage pipe, was required to pour a vertical bar. The shrinkage pipes in the several vertically cast bars extended to a depth of from 3 or 4 in. to approximately 1 in., depending upon whether the pouring was respectively fast or slow toward the finish. Each vertical bar presented four smooth faces free from the wrinkles present on the top of horizontally cast bars. After the shrinkage pipes had been removed by cropping, the bars were ready for test purposes.

In the cases of the first nine heats, no attempt was made to compare the effect of cooling the bar in air and quenching it in water. Because of the equipment used, it was most convenient to quench the horizontal bars in water immediately after solidification but to allow the vertical bars to cool in air. Later, however, the five horizontal and five vertical bars from heats 10 to 14 inclusive were cooled in air and the five horizontal and five vertical bars from heats 15 to 19 inclusive were quenched in water immediately after solidification. No material differences in properties were detected between the bars cooled in air and those quenched in water. Incidentally, this point is of commercial interest in that it indicates no metallurgical advantage in maintaining the cooling water at any particular temperature.

The chemical composition of the metal used throughout this investigation was:

	PER CENT.		PER CENT.
Copper plus silver	99.94 ± 0.02	Antimony	0.002
Silver	less than 0.003	Tin	0.001
Lead	less than 0.004	Bismuth	0.0001
Sulfur	less than 0.002	Undetermined, largely Oxygen	0.05
Arsenic	· Nil		

The horizontal and vertical bars were hot-rolled from 4 by 4 in. cross-section to rod of $\frac{1}{4}$ in. dia., in 14 reductions. The lengths of rod were processed into wire and samples were tested, representing the bottom, center and top sections of the vertical bars, and the center of the horizontal bars.

DENSITY

Density determinations were made on the as-cast and hard-drawn samples from all of the vertically and most of the horizontally cast bars. Samples for density determinations on the as-cast metal were selected from the bottom, center and top portions of each vertical bar and from midway between the ends of each horizontal bar. All samples were triangular sections, weighing approximately 25 g. each, cut from a corner edge of the bar at the respective locations. The samples of the horizontal bars were cut from one of the bottom edges. Samples for density determinations on the hard-drawn material consisted of lengths of No. 11 B. & S. gage wire drawn cold from rod of $\frac{1}{4}$ in. dia. by the following die reductions shown as diameters in decimals of an inch: 0.250, 0.204, 0.181, 0.157, 0.133, 0.114, 0.102, and 0.090. The results are summarized in Table 1.

TABLE 1.—*Density*

Heat No.	Density of As-cast Vertical Bars			Density of As-cast Horizontal Bars	Density of Hard-drawn Wire from Vertical Bars			Density of Hard-drawn Wire from Horizontal Bars
	Bottom	Center	Top		Bottom	Center	Top	
1	8.90	8.80	8.68	no sample	8.91	8.90	8.84	no sample
2	8.87	8.84	8.76	no sample	8.91	8.91	8.91	no sample
3	8.84	8.74	8.70	no sample	8.92	8.89	8.87	no sample
4	8.88	8.79	8.74	no sample	8.92	8.88	8.90	no sample
5	8.87	8.80	8.67	8.69	8.91	8.90	8.92	8.92
6	8.87	8.80	Lost	8.64	8.89	a	Lost	8.89
7	8.89	8.80	8.75	8.68	8.90	8.92	8.90	8.91
8	8.89	8.79	8.70	8.58	8.91	8.94	8.88	8.92
9	8.84	8.79	8.70	8.68	8.91	8.89	8.92	8.91
10	8.75	8.68	8.62	8.48	8.94	8.93	8.87	8.86
11	8.80	8.74	8.69	8.63	8.93	8.93	8.89	Lost
12	8.78	8.66	8.64	8.56	8.94	8.91	8.91	8.91
13	8.81	8.73	8.64	8.51	8.94	8.91	8.94	8.91
14	8.76	8.72	8.68	8.54	8.93	8.94	8.93	8.93
15	8.76	8.66	8.59	8.56	8.90	8.91	8 93	8.94
16	8.79	8.73	8.70	8.60	8.94	8.92	8.94	8.94
17	8.81	8.64	8.67	8.48	8.91	8.92	8.92	8.93
18	8.78	8.69	8.57	8.61	8.85	8.91	8.93	8.91
19	8.86	8.69	8.67	8.56	8.93	8.91	8.89	8.93
Average	8.83	8.74	8.68	8.59	8.92	8.91	8.91	8.92

a Erratic result obtained. Sample for a check test not available, so result has been omitted.

These density determinations show that copper cast horizontally is not as dense as that cast vertically. Incidentally, these determinations on the density of horizontally cast copper agree with previously published

data on the density of tough-pitch copper.[3] It is to be noted that all bottom and center sections of vertically cast bars are more dense than the corresponding horizontal bars. Comparing the densities of the horizontal bars with the top sections of the vertical bars (the top section is the least dense section of a vertical bar) there are only two top sections that are less dense than the corresponding horizontal bars and in each of these two instances the difference is within experimental error. The authors believe that this increased density is one of the factors tending to make vertically cast wire bars superior to horizontally cast wire bars.

The increased density of a vertically cast wire bar is probably due to the increased pressure exerted by the column of molten metal during solidification. In casting a horizontal bar, the height of the molten column may be as much as 4 in., therefore the pressure on the column may be considered one atmosphere. In casting a vertical bar, the height of the molten column may be as much as 60 in.; therefore the pressure varies from one atmosphere at the top, as in the case of the horizontal bar, to possibly more than two atmospheres at the bottom. This increased pressure toward the bottom very likely causes: (1) increased solubility, or possibly it should be called decreased insolubility, of the gases in the molten metal, and (2) a reduction in the volume occupied by the insoluble gas. From either or both causes, more dense copper would be expected toward the bottom of a vertically cast bar and, conversely, the degree of porosity should increase toward the top of the bar. These statements are in accord with the data presented.

It is also interesting to note that regardless of the as-cast metal density, the density of the cold-drawn No. 11 B. & S. gage wire is practically the same—8.91—in all cases, regardless of the as-cast copper density, and approximates that of the lower section of a vertical bar.

ELECTRICAL CONDUCTIVITY

Electrical conductivity determinations were made on meter lengths of annealed No. 11 B & S. gage wire obtained from $\frac{1}{4}$-in. rod by die reductions shown in the preceding section. The wire was electrically annealed for 24 sec. by suspending between two terminals a 5-ft. length of the wire through which was passed an electric current at a constant voltage of four volts. The current required was approximately 200 amp. at the beginning and decreased to approximately 100 amp. in the 24 sec. The heated wire was allowed to cool in air, which results in a slight surface tarnish. The results shown in Table 2 are averages of three determinations each.

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[3] W. R. Webster, J. L. Christie and R. S. Pratt: Some Comparative Properties of Tough-pitch and Phosphorized Copper. *Proc.* Inst. of Metals Div., A. I. M. E. (1927) 233.

TABLE 2.—*Electrical Conductivity*

(Per Cent. International Standard)

Heat No.	Vertical				Hori-zontal	Change Due to Vertical Casting (Based on Average)
	Bottom	Center	Top	Average		
A[a]				100.6	100.3	+0.3
B[a]				100.3	100.1	+0.2
C[a]				100.1	100.1	
D[a]				100.4	100.1	+0.3
1	100.3	100.2	100.2	100.2	99.9	+0.3
2	100.4	100.2	100.3	100.3	99.9	+0.4
3	100.4	100.2	100.2	100.3	99.8	+0.5
4	100.1	100.1	100.1	100.1	100.1	
5	100.4	100.8	100.5	100.6	100.2	+0.4
6	100.3	100.4	Lost	100.35	100.3	+0.05
7	99.8	100.3	100.1	100.1	100.0	+0.1
8	100.3	100.6	100.4	100.4	99.9	+0.5
9	100.0	100.3	100.2	100.2	100.1	+0.1
10	100.1	100.5	100.5	100.4	100.6	−0.2
11	100.1	100.2	100.5	100.3	Lost	
12	100.1	100.3	100.1	100.2	99.8	+0.4
13	100.3	100.6	100.5	100.5	100.3	+0.2
14	100.6	100.5	100.5	100.5	100.3	+0.2
15	100.3	100.5	100.6	100.5	100.2	+0.3
16	100.4	100.6	100.3	100.4	100.2	+0.2
17	100.6	100.6	100.6	100.6	100.4	+0.2
18	99.9	100.1	100.4	100.1	100.2	−0.1
19	100.5	100.6	100.8	100.6	100.6	
Average.....	100.27	100.40	100.38	100.35	100.15	+0.20

[a] Preliminary test bars. The location within the vertical bar from which the wire sample was obtained was not recorded.

One of the most interesting facts disclosed by the investigation is the consistently higher electrical conductivity exhibited by vertically cast bars. It is true that in two instances the conductivity of the horizontal bar is slightly higher than the corresponding vertical bar. However, it should be mentioned that on selecting and processing horizontal bars for check tests, in each of the two instances the check bar gave a result lower than the vertical bar. The check results are not shown because these bars were not necessarily taken from the same part of the heat and there is a possibility that they are not truly comparable with the vertical bars. They are mentioned to show that the trend toward higher conductivity, while somewhat small, is decidedly in favor of the vertical casting. It would seem that the conductivity data shown in Table 2 point the way toward further investigation to obtain improved electrical conductivity of commercial copper.

This conclusion is given further support by the slight but positive advantage in conductivity in favor of the center section of the vertical bars. In other words, it is the authors' opinion that, considering experimental error, the conductivity of copper wire will vary directly with the density of the as-cast metal.[4]

TENSILE STRENGTH AND ELONGATION

Table 3 contains the tensile strength and elongation (after low-temperature anneal) results obtained on the test samples. Where the result is termed "XS" it indicates an excessive number of breaks, and that the copper was not suitable for drawing, by the die set-up, into test wire.

The determinations of tensile strength were made on cold-drawn No. 11 B. & S. gage wire samples, obtained from the rolled rod by the

TABLE 3.—*Tensile Strength and Elongation*

Heat No.	Tensile Strength, Lbs. per Sq. In.				Elongation in 10 In. after Low-temperature Anneal, Per Cent.			
	Vertical			Horizontal	Vertical			Horizontal
	Bottom	Center	Top		Bottom	Center	Top	
1	64,433	64,766	63,900		23.1	23.5	22.0	24.0
2	64,466	65,033	63,466		22.6	23.6	22.3	23.5
3	63,866	65,200	65,166	•	24.5	23.5	XS	25.5
4	64,266	66,062	65,800		22.6	25.0	XS	26.5
5	65,166	64,666	63,033	65,333	23.8	23.3	24.1	25.0
6	64,433	64,100	Lost	65,066	23.8	24.8	Lost	24.5
7	64,133	64,900	65,166	63,166	23.8	22.3	24.6	24.1
8	64,966	64,466	62,900	65,400	25.0	24.1	25.3	21.5
9	64,466	64,433	64,266	64,333	22.3	25.0	22.8	25.0
10	66,250	68,200	67,050	66,450	22.5	24.5	23.5	25.0
11	67,300	67,900	68,300	Lost	25.5	25.5	26.0	Lost
12	66,700	65,800	68,950	66,700	26 5	26.0	23.5	22.0
13	67,600	65,800	64,700	69,300	23.0	27.5	25.0	23.0
14	66,500	68,400	67,650	67,650	23.5	23.0	23.5	23.0
15	67,100	58,600	56,020	67,000	25.5	26.0	24.0	23.5
16	65,600	63,400	65,200	69,400	26.5	25.0	26.0	23.0
17	66,350	67,900	67,800	66,750	27.0	22.0	XS	18.0
18	66,700	67,200	67,600	65,450	21.0	21.5	XS	XS
19	68,800	67,000	67,600	66,200	23.0	24.5	18.0	22.0
Average	65,742	65,570	65,254	66,300	24.0	24.3	less than 23.6	less than 23.4

[4] This opinion agrees with that reached by G. Masing and C. Hasse: Production of Copper of High Electrical Conductivity. *Wiss. Veroeff.* a. d. Siemens-Konzern (1928) **7**, 321.

die reductions shown under the section on Density. The wire was not annealed.

The elongation determinations were made on No. 30 B. & S. gage wire samples which were obtained by cold-drawing some of the No. 11 B. & S. gage wire prepared for tensile-strength determinations, to No. 30 B. & S. gage by single gage number reductions. The final wire samples were annealed for 2 min. at 300° C. This is a special test used to indicate response to low-temperature anneal.

These data indicate that (1) the tensile strength values obtained on vertically cast copper are slightly lower than those obtained on horizontally cast copper, and (2) slightly higher elongation values (after low-temperature anneal) are obtained on wire made from vertically cast copper.

WORKABILITY

A satisfactory test for evaluating the amenability of a given piece of copper to the commercial method of wire-drawing is a difficult matter, although an experienced wire-drawer usually is able to say whether or not various coppers are easy or difficult to draw. Possibly it is intuition that guides his statement; certainly it seems so at times. In this study to evaluate the workability of vertically cast copper as compared with that of horizontally cast copper, the number of breaks that occurred while drawing a definite quantity of rod were noted. As in the section on Tensile Strength, the term XS denotes an excessive number of breaks and that the copper was not suitable for drawing into test wire. Because of the inability to determine whether breaks were due to quality of copper or to some other reason, this information is not nearly as significant as the fact that in several instances the wire became brittle and further drawing could not be accomplished. Obviously, the copper that became brittle was inferior in quality to that which remained soft enough to draw. In order to obtain data as comparable as possible under the conditions on this part of the study, the same die reductions (single B. & S. gage numbers) and the same kind of drawing lubricant were used. The results obtained are shown in Table 4.

These data by themselves do not tell the complete story with respect to the comparative workability of the wire samples tested. For example, the data show that some of the bottom sections of the first vertical bars broke frequently. However, since most of those breaks occurred while drawing to coarse sizes of wire, it is believed that they were due to a physical condition of the cast metal, such as invisible cold shots and folds, which most likely can be corrected with improved casting·technique. Ignoring the recorded number of breaks altogether, it was unmistakably noted during the drawing operations that the

samples from the bottom and center sections of the vertical copper could be drawn more easily than those from the top vertical and horizontal samples. In other words, the wire-drawer's "intuition" caused him to be decidedly in favor of drawing wire from dense as-cast copper.

TABLE 4.—*Work ability*

| Heat No. | Number of Breaks on Vertical Bars | | | | | | | | | Number of Breaks on Horizontal Bars | | |
| | Bottom | | | Center | | | Top | | | | | |
	0.250 Rod to 11 Gage	11 to 22 Gage	22 to 30 Gage	0.250 Rod to 11 Gage	11 to 22 Gage	22 to 30 Gage	0.250 Rod to 11 Gage	11 to 22 Gage	22 to 30 Gage	0.250 Rod to 11 Gage	11 to 22 Gage	22 to 30 Gage
1	2	0	0	0	1	1	0	0	0	No sample		
2	1	0	.0	0	1	0	0	0	0	No sample		
3	2	0	0	0	0	0	2	0	XS	No sample		
4	3	0	0	0	0	1	0	0	XS	No sample		
5	4	0	1	0	0	0	0	0	0	No sample		
6	10	0	0	0	0	1	0	0	Lost	No sample		
7	10	0	0	0	0	0	0	0	0	No sample		
8	10	0	0	2	0	0	0	0	0	No sample		
9	0	0	1	0	0	1	0	0	0	No sample		
10	0	0	0	0	0	2	0	1	2	0	0	0
11	0	0	0	0	0	0	0	0	0	Lost	Lost	Lost
12	0	0	2	0	0	1	0	XS	XS	0	0	XS
13	0	2	0	0	1	2	0	0	2	0	1	2
14	0	0	0	0	1	0	0	1	0	0	1	1
15	0	1	0	0	1	1	0	0	1	0	0	2
16	0	0	1	0	0	1	0	0	XS	0	0	XS
17	0	0	2	0	0	2.	0	0	XS	0	0	2
18	1	3	1	1	0	1	0	1	XS	0	2	XS
19	0	2	0	0	1	0	0	0	0	0	0	1

In general, the data indicate that (1) the bottom and center sections of vertically cast copper can be drawn into wire more satisfactorily than the top section of vertical copper, (2) the denser copper of vertical bars free from surface defects lends itself more readily for processing into fine wire than horizontally cast bars. There seems to be no evidence against and some evidence in favor of the denser vertical bars fulfilling this requirement more satisfactorily than horizontal bars. In commercial practice it might be found advisable to modify the laboratory procedure by cropping off a portion of the top of the vertical bar to eliminate the more porous section. However, if coarse size wire is desired, the porosity should not be objectionable from a workability standpoint and in this case the top section could be diverted for this purpose. It is believed that in this way a more efficient fabrication of the copper bar could be effected than is possible with a horizontal bar

CONCLUSION

The findings of this investigation may be summarized as follows:

1. Vertical casting provides a method of producing copper wire bars which have no wrinkles and oxygen segregation on any long face.

2. Vertically cast copper appears preferable to horizontally cast copper for purposes of wire manufacture.

3. Vertically cast copper is more dense than horizontally cast copper. As would be expected, the bottom of a vertically cast copper bar is most dense, the center less dense, and the top least dense. Regardless of the initial density or method of casting, the density after cold working is approximately 8.91.

4. Wire from vertically cast copper has slightly lower tensile strength than that from horizontally cast copper.

5. Wire from vertically cast copper has a slightly higher per cent. elongation after low-temperature anneal than that from horizontally cast copper. In this regard it is probable that wire produced from the most dense as-cast metal will have the greatest elongation, notwithstanding some of the present experimental results to the contrary.

6. The electrical conductivity of vertically cast copper is higher than that of corresponding horizontally cast copper. The average increase shown by these tests is approximately 0.20 per cent.

7. Vertically cast copper apparently lends itself more readily to processing under wire-mill conditions than horizontally cast copper. The center section of a vertical bar can be processed satisfactorily to both coarse sizes and fine sizes. The top can be processed satisfactorily to coarse sizes, but not so satisfactorily to fine sizes. While the data indicate that the bottom can be processed satisfactorily to fine sizes, but not so satisfactorily to coarse sizes, it is believed that the latter finding is probably due to experimental conditions and can be corrected by modifications in casting technique.

The greatly increased speed being adopted for drawing copper into wire will require copper possessing improved properties. This study indicates that this can be accomplished at least in part by adopting vertically cast wire bars. This change, of course, will necessitate modification in casting technique at the refinery and in rolling technique at the rod mill.

DISCUSSION

S. SKOWRONSKI, Perth Amboy, N. J.—In practically all copper shapes, the density of the copper is greater at the bottom of the casting than at the top. The oxygen content also varies and is lower at the bottom than at the top. Since oxygen has a marked effect on the conductivity of copper, it is possible that the increase in conductivity noted by the authors with a vertical casting may be due to lower oxygen content.

An increased oxygen content of 0.013 per cent. will lower the conductivity by 0.20 per cent. and differences of as much as 0.010 of oxygen between a vertical and a horizontal casting can be noticed readily.

The distribution of oxygen in a cast copper wire bar has been well shown by F. W. Harris,[5] and oxygen determinations on the two type of castings would probably have shown the authors that the difference in conductivity was due to difference in oxygen content rather than to the difference in density of the original castings.

H. M. SHEPARD, Maurer, N. J.—In reading over this paper I have become very curious from the viewpoint of a copper refiner as to how much extra the wire-mill man is willing to pay for these vertically cast bars. We know what premium is paid for billets. I wonder if he is willing to pay that much for wire bars. I doubt it very much. If, as the authors suggest, the copper refineries go to open-hearth and blooming-mill practice, about which I know very little, I am afraid the capital expense would be altogether too high to be borne by the comparatively small tonnage of even the biggest copper refinery.

W. A. SCHEUCH, Chicago, Ill.—One of the problems of the copper refiner seems to be to eliminate either some or all of the gas in solid copper. At least the results in this paper indicate that dense copper, such as the bottom portion of a vertically cast ingot, is desirable. It may be possible to obtain this condition by the addition of a harmless reagent to the molten metal, such as is being done at present in the steel industry.

Economies in casting large vertical ingots and rolling them in large tonnages adjacent to the source of manufacture might lie in the freight savings, which could be effected through a direct distribution of the product to the wire mill.

W. F. GRAHAM, Mansfield, Ohio.—The paper does not include a drawing of the mold, but apparently, from the description on page 339, it is a straight-sided mold; and approaching the subject not from the standpoint of casting copper but from an experience in casting other types of non-ferrous alloys as well as ferrous alloys, I am wondering why more attention is not directed to the mold design in order to take advantage of the possible benefits of vertical casting. In other words, the differential freezing due to heavier mold sections on the bottom, lighter mold sections on the top; the old argument of big end up versus big end down, and the effect of mold taper, all have an influence in the physical characteristics of the ingot or the products from the ingot.

A study of this matter could very well include those factors. Of course, copper is not a dead-melted material, and taking into account the higher shrinkage it may not react as do other types of materials.

J. W. SCOTT.—Mr. Skowronski's point on the variation of the electrical conductivity with the oxygen content of the copper no doubt is worthy of consideration. Microscopic examination of samples from various parts of the ingots showed practically uniform oxygen content, although it must be admitted that slight differences in oxygen content are hard to detect with the microscope. Possibly chemical analyses,

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[5] F. W. Harris: Distribution of Tensile Strength in Hard-drawn Copper Wire. *Proc.* Inst. Metals Div., A. I. M. E. (1928) 520.

which were not made, would have shown the differences suggested. However, from the Bridgeman theory, it may be deduced that the electrical conductivity of a metal varies directly with the density, and such has been our finding. We do not attempt to state definitely whether the increased conductivity of the bottom portion of an ingot is due to difference in oxygen content or density; it may be due to both.

Mr. Graham is correct no doubt in assuming that some particular mold design will produce the best copper ingot, but we did not enlarge our investigation to determine this point. In our experiments, we used a straight-sided mold, since it was what we had at hand, and our principal concern in casting the vertical bars was to maintain the same ratio of mold to bar weight as was used in casting horizontal copper wire bars.

In this experimental work, we have not devoted much study to the economic questions involved. However, I believe Mr. Shepard's comment might leave a wrong impression because from it one might believe that steel-mill practice, where large vertical ingots are cast and rolled, may be more expensive than copper-mill practice where small ingots are cast and rolled. It is my understanding that steel-mill practice is the cheaper, on a unit weight of output basis. It is true that large tonnages of copper would have to be handled at any one mill but with present day trends in the integration of the copper industry, the necessary tonnages might be obtainable.

A Theory Concerning Gases in Refined Copper*

By A. E. Wells,† Cambridge, Mass., and R. C. Dalzell,‡ Roselle, N. J.

In 1866, Thomas Graham[1] called attention to the volume of gases, three times the volume of the sample, evolved from a meteoric iron heated in an evacuated porcelain tube. From that time to this the occurrence and significance of gases in metals have been the subject of investigation by many workers, among whom Sieverts,[2] Iwasé[3] and O. W. Ellis[4] stand preëminent.

Sieverts and Iwasé concerned themselves with the solubility of a number of gases in metals in the liquid and solid states. They determined the absorption coefficients of these gases, and in all cases found a sharp change in solubility at the melting point of the metals. Ellis analyzed the gases evolved by solidifying copper and those occluded by the solidified metal.

Lobley and Jepson[5] endeavored to determine the effects of hydrogen, carbon monoxide and nitrogen on the porosity of copper that was allowed to solidify in the presence of each gas after 30 min. exposure to it in the

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* Contribution from the Metallurgical Laboratory at Harvard University.

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‡ Research Department, American Smelting & Refining Co.

[1] T. Graham: On the Occlusion of Hydrogen Gas by Meteoric Iron. *Proc. Royal Soc.* (1867) **15**, 502.

[2] A. Sieverts: Zur Kenntnis der Okklusion und Diffusion von Gasen durch Metalle. *Ztsch. f. Physik. Chem.* (1907) **60**, 129.

A. Sieverts und J. Hagenacker: Über die Löslichkeit von Wasserstoff und Sauerstoff in festem und geschmolzenem Silber. *Ibid.* (1909) **68**, 115.

A. Sieverts und J. Hagenacker: Ueber die Absorption des Wasserstoffs durch metallisches Nickel. *Berichte* Deut. Chem. Gesell. (1909) **42**, 338.

A. Sieverts und W. Krumbhaar: Über die Löslichkeit von Gasen in Metallen und Legierungen. *Ibid.* (1910) **43**, 893.

A. Sieverts und E. Jurisch: Platin Rhodium und Wasserstoff. *Ibid.* (1912) **45**, 221.

A. Sieverts und E. Bergner: Versuche über die Löslichkeit von Argon und Helium in festen und flussigen Metallen. *Ibid.* (1912) **45**, 2576.

[3] K. Iwasé: Occlusion of Gases by Metals and Alloys in Liquid and Solid States. *Sci. Repts.* Tohoku Imp. Univ. [1] (1926) **15**, 531.

[4] O. W. Ellis: Absorbability of Gases in Casting Copper and Effect of Adding Cuprosilicon. *Trans.* A. I. M. E., Inst. Metals Div. (1929) 443; Gases in a Sample of Overpoled Fire-refined Copper. *Ibid.*, 470.

[5] A. G. Lobley and D. Jepson: Influence of Gases on Copper at High Temperatures.—Pt. I. *Engng.* (1926) **121**, 380.

liquid state. Unfortunately, they used graphite crucibles. Caron[6] observed that the permeability of graphite permitted the escape of occluded gases during solidification. The results of the experiments of Lobley and Jepson seem, therefore, to be of questionable value.

TYPES OF COPPER TESTED

Although present experiments have been along the line of those performed by Lobley and Jepson, the phenomenon described by Caron has been recognized. In fact, it has been utilized to distinguish between solubility in deoxidized copper and solubility in ordinary commercial copper (oxygen = 0.06 per cent.).

Two types of copper were used in these experiments, referred to herein as deoxidized and oxidized copper. Experimental data are given in Table 1.

TABLE 1.—*Experimental Data*

Summary of Melts

Series	Crucible	Metal	Gas	Time Exposed
1	Graphite	Deoxidized Copper having density of 8.96	H_2	3 hr.
			CO	3 hr.
			CO_2	3 hr.
			N_2	3 hr.
2	Vitreosil	Deoxidized Copper having density of 8.96	H_2	3 hr.
			CO	3 hr.
			CO_2	3 hr.
			N_2	3 hr.
			H_2O	3 hr.
3	Graphite	Oxidized Copper having density of 8.95	H_2	5 min.
			CO	2 hr.
			CO_2	3 hr.
			N_2	3 hr.
4	Graphite	Ingots from 1, 2 and 3	vacuum	2 hr.

Gas	Densities of Ingots			Average Density
	Series 1			
CO_2.	8.96	8.97	8.95	8.96
CO.....................	8.98	8.96	8.96	8.97
N_2.....................	8.82	8.85	8.83	8.83
H_2.....................	8.97	8.98	8.97	8.97

No gas tested had any effect except nitrogen, which caused porosity in each ingot made in its presence.

[6] M. Caron: De l'absorption de l'hydrogene et de l'oxyde de carbone par le cuivre en fusion. *Compt. rend.* (1866) **63,** 1129.

TABLE 1.—(Continued)

Gas	Densities of Ingots			Average Density
Series 2				
CO₂.....................	7.06	6 84	6.91	6.94
CO....	8 05	8 22	8.28	8.18
N₂.....................	8 83	8.83	8.86	8.84
H₂O.............	8.85	8.80	8.83	8.83
H₂.....................	8.94	8 93	8.93	8.93
Series 3				
CO₂.....................	8.96	8.94	8.95	8.95
CO.....................	6.30	6.51	6.37	6.39
N₂.....................	8.82	8.80	8.80	8.81
H₂.....................	6.71	7.43	6.66	6.60

Series 4

Original Series	Original Gas	Original Average Density	Average Density of Remelted Ingot
1	N₂	8.83	8.95
2	CO₂	6.94	8.95
2	CO	8.18	8.97
2	N₂	8.84	8.95
2	H₂O	8.83	8.94
2	H₂	8.93	8.95
3	CO	6.39	8.94
3	N₂	8.81	8.94
3	H₂	6.60	8.95

The first type of copper was prepared by melting carefully cleaned refined series cathodes in a graphite crucible in the presence of hydrogen. The gas was replaced every 4 hr. The gas removed at the end of 15 hr. exposure did not discolor lead-acetate paper. This was accepted as proof that any occluded sulfur had been completely removed by hydrogen. The small amount of cuprous oxide was likewise completely reduced. This fact was determined by microstructural examination.

The second type of copper was prepared by melting wire bar and cake drillings in vacuum. The oxygen content was about 0.06 per cent.

All the gases used were of the commercial bottled type, except the carbon monoxide; that was generated by breaking down formic acid in the presence of concentrated sulfuric acid.

The dissimilarity of the results of Series 1 and 2 of Table 1 verifies Caron's work in showing the importance of considering the crucible material in work of this nature. The second series indicates the relative effects of the various gases on the porosity of copper in which they are dis-

solved.   In order of decreasing severity of effect, they may be listed: CO_2, CO, N_2 and H_2O about equal, H_2. A careful study of Table 2 reveals the explanation for this order.

TABLE 2

Gas	Solubility at 1083° C.[a]		Volume Released on Solidification[a]	Equiv. Volume at 1083° C.[a]	Per Cent. of Volume of Copper[a]	Relative Rates of Diffusion of Gases Through Copper at 700° C.[b]
	In Liquid Copper	In Solid Copper				
H_2	11.45	8	3.5	16.2	145	1000
H_2O						65
CO	24	3	21	97.2	873	17
CO_2	19.5	1.5	18	83.3	748	0.6
N_2	3.5	0.0	3.5	16.2	145	0.0

[a] K. Iwasé: *Op. cit.*

[b] N. B. Pilling: Action of Reducing Gases on Hot Solid Copper. *Trans.* A. I. M. E. (1918) **60**, 322.

Carbon dioxide has the greatest effect because of (1) the large amount of it evolved on solidification and (2) its low rate of diffusion through copper after solidification.

More carbon monoxide than carbon dioxide is released on solidification, but solid copper at 700° C. (and probably higher temperatures) is more than 28 times as permeable to carbon monoxide, hence the effect is less.

Only one-sixth as much nitrogen is evolved as carbon monoxide, but the rate of diffusion of nitrogen at 700° C. is 0.0, hence practically all that is evolved is retained and therefore effective in lowering the density.

Water diffuses through copper at a rate about 3.8 times that of carbon monoxide at 700° C.   The amount of it evolved on solidification must be fairly large, as its effect on porosity is about the same as that of nitrogen.

The rate of diffusion of hydrogen is so great, and the amount of it evolved so small (relatively), that its effect on porosity is almost negligible.

The melts of the third series were made in the graphite crucibles with the object of determining the effect of cuprous oxide on retention of gases in solution.

If, in the presence of cuprous oxide, the same results were obtained as in series 1, the inference would be that the gases had been dissolved in the same manner as in the deoxidized copper.   On the other hand, if the ingots in this third series showed porosity, it would be evident that there existed some different state of dispersion which did not permit escape of gases rapidly enough to prevent formation of blowholes.

The ingots of series 3 made in the presence of hydrogen and of carbon monoxide were very porous; those made in the presence of nitrogen showed the same porosity as before, and those subjected to carbon dioxide were as dense as those made in series 1.

Only a 5-min. exposure to hydrogen and a 2-hr. exposure to carbon monoxide were allowed in the liquid state, as appreciable reduction of the cuprous oxide was not desired.

Water could not be experimented with in this series because of its reaction with hot graphite, but its action should be expected to be similar to that of carbon dioxide.

The third series of experiments indicates that the carbon dioxide and water formed by partial reduction of dissolved cuprous oxide are in a state of dispersion quite different in the liquid metal from that of carbon dioxide and water which are dissolved as such.

COLLOIDAL DISPERSION OF CUPROUS OXIDE

The theory advanced by the writers to explain the foregoing important phenomenon is that cuprous oxide is colloidally dispersed in molten copper and in that state has the property of adsorbing water and carbon dioxide. A strong indication of the validity of this theory would be the ability to explain by its use other phenomena observed in the melting and casting of copper. It will be shown that the theory meets this requirement, but first the fundamental soundness of it from general considerations must be examined.

Metallographists have usually assumed that if a eutectic is found in a binary system of alloys, the two components of the system are soluble in the liquid state, but insoluble in the solid. This assumption is due to the analogy presented by the phenomena observed in the solution of a solid or a liquid in another liquid at normal temperatures. The freezing point of the solvent may be lowered by the addition of the solute, up to a certain composition. Beyond that concentration, further addition of solute raises the freezing point. Where this sequence of effects occurs, the solute is usually molecularly dispersed in the liquid solvent, but on solidification the two components are found to be mutually insoluble (partially or completely).

However, it is an established fact that a colloidally dispersed substance may depress the freezing point of the dispersing medium. The effect is slight at ordinary temperatures, so this class of dispersion apparently was disregarded by metallurgists for a long time. With the advancement of the knowledge of colloids, however, came realization that numerous metallurgical phenomena might profitably be considered as due to colloidal dispersion.

The concept of most interest in the present connection relates to the "modification" of aluminum-silicon alloys by addition of minute amounts of sodium. The aluminum-silicon series has a eutectic at about 11 per cent. silicon under normal conditions, freezing at 577° C. Naturally the molten mixture was considered to be a true molecular solution.

That sodium is insoluble in solid aluminum and silicon, all investigators agree. A series of aluminum-silicon alloys may be prepared, ranging in silicon content from about 10 per cent. to 16 per cent., and about 0.02 per cent. of sodium added to each in the liquid state. If the temperature of each is then raised to 804° C., held there a certain length of time, and the metal cast, the eutectic composition is then at about 15 per cent. silicon, and the eutectic freezing point has been reduced to 564° C. The silicon is in a much finer state of dispersion. An analysis will show only a trace of sodium remaining in the alloy. Evidently the sodium acted as a peptizing agent. The silicon was probably originally in a coarse colloidal state, but the sodium increased its dispersion markedly. It must be remembered that the colloidal chemistry of molten metals may possibly deal with much larger particles than would be heretofore considered as of colloidal dimensions.

With this evidence of a coarse colloidal condition in what was thought to be a molecular solution, there can be little hesitancy in assuming cuprous oxide to be colloidally dispersed in molten copper.

ADSORPTION OF GAS BY COLLOIDAL PARTICLES

All solids tend to adsorb any gases or vapors with which they are in contact. In so far as adsorption is accompanied by an evolution of heat, the amount of adsorption must decrease with rising temperature. This is found to be the case experimentally, but the change is often a very small one. In some cases there is apparently a large increase in adsorption with rising temperature.

Therefore, it may be assumed that the colloidal particles of cuprous oxide in molten copper may adsorb any gases that are dispersed in the copper, or that they may come in contact with at the surface of the bath. Further, some gases may be adsorbed in increasing amounts as the temperature rises, whereas the reverse may be true of others.

Adsorption is a surface phenomenon, so it is but natural to expect a definite saturation point for any one gas adsorbed on a particular adsorbent at one temperature and pressure. That is, there will be a limit to the amount adsorbed per unit of surface. The more finely divided the adsorbent, the greater will be its gross surface area, and hence its gross adsorbing power.

If a number of particles, each of which is saturated, agglomerate, the superficial surface and hence the gross adsorbing power will be reduced. When this occurs, the excess adsorbed material will be liberated. When a colloidal solution is actually frozen solid, the colloid *may* agglomerate and thereby reduce the adsorption capacity.

If the cuprous oxide particles agglomerate on solidification of the melt, the resulting particles may not be capable of retaining the total adsorbed gas. This will be released, forming gas pockets. This always occurs to some extent when copper containing cuprous oxide is allowed to solidify.

Table 2 indicates that carbon dioxide and water have a relatively low rate of diffusion in solid copper at 700° C. This and other observations warrant the assumption that the rate of diffusion of these two gases is also relatively low in molten copper, hence one would expect little adsorption of these gases on cuprous oxide when they have been dissolved as such.

Explanation of Gaseous Phenomena in Casting Refined Copper

Throughout the blowing and poling periods, there is a continouus increase in porosity (Fig. 1). The rate of increase is greater during blowing, being particularly accelerated near the end of the poling period.

The bath is doubtless saturated with nitrogen from the compressed air used for blowing. Water and carbon dioxide are also present in the compressed air, but in relatively small amounts. The dissolving of nitrogen is probably the principal factor in increasing the porosity during
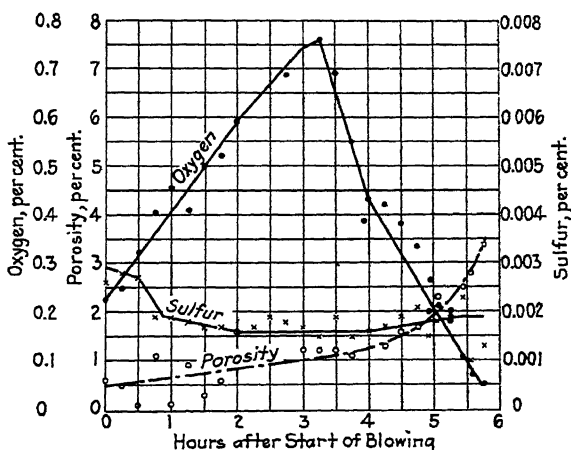
Fig. 1.—Porosity curve in casting refined copper.

blowing. It has been shown that this gas causes porosity in solid copper regardless of the cuprous oxide content of the molten copper in which it is dissolved.

The cuprous sulfide content decreases during blowing. Apparently sulfur dioxide gas caused by reaction of the cuprous sulfide and cuprous oxide in the grain boundaries is of no consequence as far as porosity is concerned, for the porosity seems to increase at a steady rate during blowing.

During poling, each particle of cuprous oxide is attacked by reducing gases, forming carbon dioxide and water at the surfaces of the particles, where they are held by adsorption.

As reduction is continued, each particle decreases in size. At the same time its load of carbon dioxide and water increases. Saturation is approached, and accordingly agglomeration on solidification releases increasingly larger amounts of gas. The porosity increases rapidly.

On solidification, then, porosity is caused: (1) By gases which have been held in solution in molten copper and liberated on solidification; (2) by gases adsorbed at the surface of cuprous oxide particles and liberated as the surface area of the cuprous oxide is reduced by agglomeration.

When reduction is stopped at the proper point, the evolved gases distend the casting just the necessary amount to give the desired "set."
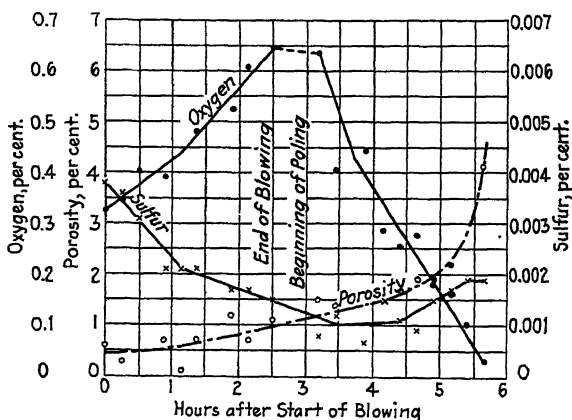
Fig. 2.—Porosity curve in casting refined copper.

Copper may be held at this point in the furnace for several hours, but the set very gradually rises, due perhaps to slow agglomeration of the cuprous oxide particles in the molten bath.

The accepted explanation of conditions prevailing at "tough pitch" has been that the solidification shrinkage of the cuprous oxide was just sufficient to balance the distending effect of the gases. This is not logical, as there is no evidence to prove that copper containing cuprous oxide will have a greater solidification shrinkage coefficient than that of pure copper. The present theory explains the situation much more satisfactorily. It is the solidification shrinkage of the copper itself that is balanced by the distending effect of the gases.

When reduction is continued beyond the desired point (overpoled), the cuprous oxide particles are reduced to such a small size that each one is probably saturated, with the result that the volume of gases evolved on agglomeration is too large to be contained within the shape.

Slight reoxidation will not rectify the overpoled condition. New particles of cuprous oxide are created, but there is slight chance of their

coming in contact with the old particles. The saturated condition of the old particles, therefore, is not relieved.

When copper from the same ladle is poured into two molds, one of which is hotter than the other, the casting in the hotter mold will have the higher set. This is caused by the slower solidification in the hot mold. Slow solidification allows time for more agglomeration of the cuprous oxide; consequently, more gas is liberated. For the same reason, the hotter of two ladlefuls of copper from the same furnace will cast with a higher set, when both molds are at the same temperature.

Commercial deoxidized copper is practically gas-free, as evidenced by the dense castings obtained. This is to be expected, as no cuprous oxide remains to carry the gases. The slight porosity that remains is due solely to liberation of gases which were dissolved in the liquid copper.

The effect of *dissolved* gases on porosity of deoxidized copper cast in commercial shapes is much less than that effect observed in laboratory castings, because of the greater ease of escape by diffusion from the commercial shapes and because of the lower partial pressures of the gases as encountered in practice.

Absolute verification of the assumptions made is considered impossible with present apparatus, but the adaptability of the theory as derived argues for its acceptance. Heretofore, all the foregoing phenomena stood as separate entities, unexplained. It has been shown that all of them may be related to one concept—the colloidal state in molten metals.

Influence of Dissolved Sulfur on Density of Cast Refined Copper

No data have been published that settle the question as to how dissolved sulfur influences the density (and hence the set) of cast refined copper.

Siebe[7] has shown that the deleterious effect of sulfur on the properties of copper is due to the part of it that is present as dissolved sulfur dioxide. Cuprous sulfide has less effect than the same percentage of cuprous oxide.

Skowronski[8] demonstrated the value of using charcoal instead of coke as a cover during the poling and casting of refined copper. He was the first to show that the cover is an important source of the sulfur adsorbed by a charge after blowing.

His second article, published at the same time, stresses the importance of the relation between the sulfur and oxygen contents of refined copper.

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[7] P. Siebe: Einiges über den Einfluss von Schwefel auf Kupfer. *Ztsch. f. Metallkunde* (1927) **19**, 311.

[8] S. Skowronski: Oxygen and Sulfur in the Melting of Copper Cathodes. *Trans. A. I. M. E.* (1918) **60**, 307; Relation of Sulfur to the Overpoling of Copper. *Ibid.*, 312.

His data prove conclusively that the amount of cuprous oxide required for tough pitch varies as the cuprous sulfide content varies.

Stubbs[9] proved that about 70 per cent. of the sulfur dioxide dissolved in molten copper reacts to form cuprous sulfide and cuprous oxide. The 30 per cent. unaccounted for may be dispersed as other gases are.

The melts of the first series in the present experiments were made principally to provide material for the second series. It is an accepted fact that copper exposed in the liquid state to an atmosphere of concentrated sulfur dioxide forms very porous castings when allowed to solidify. The material of series 1 was deoxidized (with hydrogen) copper melted in a vitreosil crucible in the presence of sulfur dioxide gas. The densities are given in Table 3. Microstructural examination under polarized light revealed both cuprous oxide and cuprous sulfide in the ingots after this treatment

TABLE 3.—*Densities of Melts*

Series 1		Series 2			
Ingot No.	Density	Melt No.	Remelt 1	Remelt 2	Remelt 3
1	8.35	1	8.91	8.92	8.92
2	8.38	2	8.92	8.91	8.92
3	8.33	3	8.91	8.93	8.92
Avg.	8.35				

The tests of series 2 were made on ingots from series 1 remelted in vacuum in a vitreosil crucible. Remelting the ingots produced in the first series of melts increased the average density of them from 8.35 to 8.91 (Table 3). Subsequently, remelting did not increase the densities appreciably. Microstructural examination made after the third remelting operation revealed no apparent decrease in the amount of cuprous sulfide and cuprous oxide present.

The mechanism of sorption of sulfur dioxide gas in molten copper has been explained clearly by Stubbs.[9] The presence of cuprous oxide and cuprous sulfide in solid copper that had been exposed to this gas when in the liquid state is a qualitative verification of his conclusion that these compounds are formed when this gas dissolves in copper. The 30 per cent. which he does not account for is probably held in solution as are hydrogen, carbon monoxide, water, carbon dioxide and nitrogen. The phenomena are analogous.

Sulfur dioxide has always been considered to be the most troublesome gas in the casting of refined copper. The results of the second series of

[9] C. M. Stubbs: The Action of Sulphur Dioxide on Copper at High Temperatures. *Jnl.* Chem. Soc. (1913) **103**, 1445.

melts lead the writers to believe that this gas is actually of slight importance in so far as its effect on porosity is concerned. Porous ingots resulted when melts were made in the presence of sulfur dioxide, but the porosity was less than that caused by carbon monoxide (see data in preceding pages). Remelting in vacuum reduced the porosity to a very low point.

If reversal of the equation

$$6Cu + SO_2 \rightarrow Cu_2S + 2Cu_2O$$
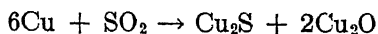
occurred when the cuprous oxide and cuprous sulfide became concentrated in the grain boundaries on solidification, porosity should be expected each time the metal was remelted and recast. This was not observed to occur, hence it may be concluded that there was little or no reaction between cuprous oxide and cuprous sulfide as they became concentrated at the grain boundaries.

On account of the reaction of sulfur dioxide gas with hot graphite, melts could not be made in graphite crucibles; therefore, no conclusion can be formed as to whether or not this gas enters into any adsorption phenomena in the molten metal, as hydrogen and carbon monoxide appear to do.

An experiment has been referred to previously[10] in which sulfur dioxide was detected in the gases evolved by a solidifying cake. This shows that at least part of the dissolved sulfur dioxide escapes by diffusion through the solid metal on solidification.

The porosity curves shown in Figs. 1 and 2 show that there is a progressive increase in porosity of solidified metal cast at short intervals throughout the blowing and poling periods. If sulfur dioxide influences porosity, there should be a change in slope of the porosity curve as soon as the sulfur content has reached its lowest value. No such change is found.

Skowronski's work shows that sulfur has a marked effect on porosity, but this need not be attributed to sulfur dioxide gas as such. There is nothing in his observations to indicate that the gas is the medium through which the sulfur exerts its effect. He simply shows that the cuprous oxide content must be higher if proper pitch is to be produced with copper containing more cuprous sulfide than its normal content.

The writers find a possible explanation for the phenomenon in the colloidal theory proposed earlier in this paper. Cuprous sulfide apparently is a coagulant for colloidally dispersed cuprous oxide in molten copper. The more cuprous sulfide present in the bath, the greater the coagulation of cuprous oxide particles; thus there is less adsorption capacity. If this is true, each cuprous oxide particle will approach saturation sooner during poling than it would if less cuprous sulfide were present. Hence, at tough pitch the oxygen content must be higher.

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[10] R. C. Dalzell: Discussion of paper by O. W. Ellis. *Trans.* A. I. M. E., Inst. Metals Div. (1929) 474.

CONCLUSIONS

1. Certain gases dissolve in molten copper with which they are in contact.

2. Parts of the dissolved gases are evolved on solidification, on account of changes in solubility at the melting point of copper.

3. Cuprous oxide in molten copper is colloidally dispersed.

4. Cuprous oxide colloidally dispersed in molten copper adsorbs certain gases.

5. Agglomeration of cuprous oxide particles on solidification liberates parts of the adsorbed gases.

6. Porosity in cast copper is caused by gases evolved from two sources in the molten copper:

a. Hydrogen, carbon monoxide, water, carbon dioxide and nitrogen are evolved on solidification due to changes in solubilities at the melting point of copper. If these five gases are at the same pressure in contact with molten copper, they may be listed as follows in the order of decreasing severity of effect on porosity *from this source:* Carbon dioxide, carbon monoxide, nitrogen, water and hydrogen. In practice, however, nitrogen probably has the principal effect *from this source,* as it constitutes about 60 or 70 per cent. of the gases in contact with the copper.

b. Water and carbon dioxide are liberated by agglomeration of colloidal cuprous oxide particles on which they are adsorbed. Hydrogen and carbon monoxide dissolved in molten copper tend to reduce any cuprous oxide that is present. The reduction products—water and carbon monoxide—are adsorbed at the surfaces of the cuprous oxide particles at which they are formed. The tendency is slight for dissolved water and carbon monoxide to *migrate* to a copper-cuprous oxide interface. Dissolved nitrogen is not adsorbed on cuprous oxide particles in molten copper.

Of the two sources, the second is by far the more important in practice.

7. Sulfur dioxide dissolves in molten copper, partly reacting with it to form cuprous sulfide and cuprous oxide.

8. In furnacing and casting refined copper, the amount of sulfur dioxide dissolved is so small that only small quantities of cuprous sulfide and cuprous oxide are produced. There is insufficient concentration of these in the grain boundaries on solidification to cause the reversal of the reaction, hence there is no appreciable evolution of sulfur dioxide from this source on solidification, and consequently no direct effect by the sulfur dioxide on the porosity of the casting.

9. Cuprous sulfide decreases the dispersion of cuprous oxide in molten copper in which both are present. The effect varies directly as some function of the concentration of cuprous sulfide (within the range of concentrations encountered in casting refined copper). Decreasing the dispersion

will decrease the adsorption capacity, hence each particle of cuprous oxide will approach saturation sooner than if the dispersion had not been reduced. Accordingly the oxygen content at tough pitch must be greater than it would be if no cuprous sulfide had been present.

DISCUSSION

C. S. WITHERELL, New York, N. Y. (written discussion).—It seems to me that the authors overlooked an opportunity to explain the apparent paradox that cuprous oxide and cuprous sulfide could exist together in the molten bath without promptly and energetically reacting on each other. The authors' adsorption theory furnishes a reason, to wit: if either the cuprous oxide or cuprous sulfide adsorbed an inert film (e. g., nitrogen), the necessary actual contact between oxide and sulfide would be prevented and hence no reaction could take place.

F. R. PYNE, Perth Amboy, N. Y. (written discussion).—In the past a number of theories have been brought forward in an attempt to explain the behavior of copper during poling and casting, but none have proved entirely satisfactory. The basis of these theories has been that copper containing oxygen has less capacity in the molten state for dissolving gases than when oxygen is absent, or present in insufficient quantity. In 1918, Mr. Skowronski, in two important papers,[11] showed conclusively that sulfur was the controlling factor in poling the charge, and thus made a definite and valuable contribution to the science of copper refining.

We now have another theory brought forward, which we may call the colloidal theory, the basis for which is that cuprous oxide is colloidally dispersed in the molten mass and in such condition absorbs gases which are released only upon exceeding the adsorption capacity of the particles. If such a theory could be substantiated it would go far towards explaining the various phenomena encountered in copper refining, but from various theoretical aspects the existence of colloidally dispersed cuprous oxide appears to be extremely doubtful.

However, it would appear that a possible explanation of the results obtained in their experiments, and one that would seem to be in accord with conditions encountered in practice, would be the assumption that the diffusion rate of the gases formed by the reduction of cuprous oxide, which are soluble in molten copper, is extremely low in the presence of cuprous oxide, and further, that this rate is further lowered by an increase in the ratio of sulfur to oxygen.

As the basis for such an assumption, it is known that copper containing a high percentage of cuprous oxide will have a heavy shrinkage when commercially cast, indicating either a comparative freedom from dissolved gases or that any dissolved gases have a high diffusion rate. As the cuprous oxide is reduced by poling, it is found that the set rises as the reduction in oxide content progresses, indicating that the rate of diffusion of the gases of reduction is low, otherwise the original shrinkage should persist.

If the sulfur content of the copper is increased, it is found that reduction of the cuprous oxide cannot be carried to the same point as before without having too high a set or else throwing a worm indicative of overpoling. This would indicate that the already low rate of diffusion has been further lowered by the presence of the sulfur.

Copper that has been deoxidized by the addition of phosphorous to the ladle will be found to have a heavy shrinkage, while copper from the same furnace that has not been deoxidized will have a full set. Inasmuch as the phosphorus deoxidizes the

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[11] S. Skowronski: *Op. cit.*

copper by direct combination with the oxygen of the cuprous oxide, there will be no gases of reduction formed that would cause the set to rise. However, at the time that the phosphorous was added there were dissolved gases present, as evidenced by the full set of the nondeoxidized copper, it is evident that the rate of diffusion of these gases has been increased by the absence of cuprous oxide.

Applying this assumption to conditions encountered in practice, it appears to provide an explanation, as may be noted from the following:

When a charge of molten copper is held in the furnace for a number of hours the set gradually rises. During this period the copper is gradually adsorbing sulfur from the fuel gases and from the charcoal or coke covering of the bath. As the amount of oxygen in the copper remains unchanged the ratio of sulfur to oxygen increases, reducing the rate of diffusion of the gases of reduction and causing the rise in the set.

When a charge of copper becomes overpoled the condition can be remedied only by reoxidizing the charge. This phenomenon has never been satisfactorily explained heretofore, but under the present assumption it would seem that the metal has become supersaturated with the gases of reduction and such a condition can be corrected only by a thorough removal of the sulfur present, which is hindering the diffusion of the gases.

Skowronski, in the paper previously referred to, claimed that in the absence of sulfur it is impossible to overpole copper. The present assumption would seem to substantiate this theory, for in the absence of sulfur there would be no tendency to restrain the rate of diffusion, and as the amount of cuprous oxide is continually decreasing, this in turn permits an increase in the rate of diffusion; a point will be reached where the rise in the set will be checked, after which there should be a shrinkage.

When casting light work a greater amount of poling is required than when casting heavy work. In light work the ratio of the exposed surface to the weight of the casting is greater than with heavy work. This increased area permits the diffusion of a greater amount of gas per unit of time per unit of weight, hence there must be an increased volume of gas per unit of weight to produce the required set. Were it not for the slow diffusion rate of the gases of reduction it would be difficult to obtain a proper set on a light casting.

When a bar is poured at one end, the end opposite the point of pouring will have a higher set than the pouring end. Previous theories do not satisfactorily account for this. As the metal cools at the end opposite the point of pouring there is a slight migration of cuprous oxide to the hotter metal. The sulfur being uniformly distributed throughout the bar would then have a higher ratio to the oxygen at that point. This higher ratio would cause a reduction in the rate of diffusion of the gases of reduction, resulting in the higher set.

When copper is cast in a hot mold the casting will have a higher set than if the same copper is cast in a colder mold. Here we have a condition of slower cooling of the metal, which permits the slow diffusion of more of the gases from the lower part of the casting to the upper portion. If the rate of diffusion of these gases was not very low, the additional time of cooling would permit the escape of a greater volume of these gases and there should be a tendency for the set to fall off instead of rising.

R. S. DEAN, Washington, D. C. (written discussion).—As the paper by Wells and Dalzell makes a most interesting and revolutionary assumption in regard to the condition of copper oxide in molten copper, it is rather unfortunate that they did not take the trouble to get any direct experimental evidence of the presence of dispersed copper oxide in molten copper. The obvious method of testing the assumption would be to determine the distribution of particle size of copper oxide in a column of molten copper under gravity or centrifugal force. If the authors' assumption is correct, it has many commercial possibilities; for example, centrifugal deoxidation of copper.

L. B. BARKER, Cambridge, Mass. (written discussion).—This paper provides a number of very interesting topics for discussion. Bolton and Weigand reduced the porosity in bronze valve castings by eliminating carbon monoxide from the atmosphere of their electric furnace.[12] An air jet was introduced into the furnace, which burned the carbon monoxide to carbon dioxide and provided an approximately neutral atmosphere. If carbon dioxide is more severe than carbon monoxide in producing porosity, what explanation can the authors offer for Bolton and Weigand's results? It has been suggested in this connection that in the absence of a reducing atmosphere certain impurities were oxidized which would otherwise have remained in the metal.

It would be interesting to know the cooling rate of the specimens used in these experiments. We can control the formation of gas bubbles by the rate and method of cooling.

If the colloid theory is to be applied to other alloys of the $Cu-Cu_2O$ type, will the colloid condition continue as the concentration of the minor constituent is increased? The concept of colloids in this case implies that the minor constituent is held in suspension in the major constituent. It is thus evident that as the concentration of the minor constituent increases a point must be reached in which the colloidal form develops into an agglomeration or is assumed by the other constituent and creates a reversal of state.

If the Cu_2O is in the form of colloids, could we not avoid the oxide network by drastic quenching? It would seem that the speed of a colloid in moving to the grain boundary would be subject to definite limitations and a speed of quenching could be provided which would hinder or totally impede this movement.

At the bottom of page 354 a statement is made to the effect that oxidized copper will have a tendency to form gas pockets on solidification. Do the authors mean that it would be easier to obtain solid metal with straight copper than with slightly oxidized copper?

C. R. HAYWARD, Cambridge, Mass.—This paper is an important contribution to an important subject; the theory deduced from the result is interesting and seems to explain certain phenomena during the casting of copper. It is unfortunate that the authors have not described the methods used in obtaining the results, for these would be helpful in determining their application under other conditions.

The bad effect of CO_2 has been pointed out but it is hard to conceive of much CO_2 being presen tin copper produced under commercial conditions. It also seems probable that most of the nitrogen, which may have entered the copper during the oxidizing period, is removed during the poling. This leaves hydrogen, CO, H_2O and SO_2 to be considered near the end of the poling operations. The authors dismiss SO_2 as being of little effect, and because of the high diffusion rates of hydrogen and water these too should have little influence on porosity. Thus by process of elimination we have CO left as the principal offender in commercial operation.

There is, however, another phase of the matter referring to commercial practice; that is, the effect of oxidation during casting. Studies in the laboratory have convinced me that molten copper low in oxygen when exposed to the air absorbs oxygen at an astonishing rate. In pouring small test bars with the metal falling only about 2 in., copper free from oxygen may take up 0.01 to 0.015 per cent. oxygen. Of course the more rapidly the copper is poured the less the absorption of oxygen; possibly at the rate of pouring in practice it is not serious, but it must take place to some extent. During the later stages of poling there is appreciable absorption of sulfur by the bath, much of which reports as Cu_2S. It is my opinion, which unfortunately I cannot support by experimental data, that during casting considerable copper is oxidized to

[12] J. W. Bolton and S. A. Weigand: Incipient Shrinkage in Some Non-ferrous Alloys. *Trans.* A. I. M. E., Inst. Metals Div. (1929) 475.

Cu_2O which in turn reacts with CO to produce CO_2 and with Cu_2S to produce SO_2 and that these gases evolved during the solidification period are the principal causes of the phenomena observed when copper is overpoled.

The lower the oxygen in the copper at the time of casting, the more sulfur and CO is contained in it, and also the more readily is it oxidized, consequently producing more SO_2 and CO_2.

I am not disposed to dispute the adsorption theory advanced by the authors; the ideas mentioned above are not in conflict with it.

C. G. MAIER, Berkeley, Calif. (written discussion).—The hypothesis of these authors that cuprous oxide is colloidally dispersed in molten copper will be astonishing to chemically trained metallurgists. The solution of cuprous oxide in copper behaves so normally in approaching that of a perfect solution, for which Raoult's law holds, that the melting diagram could be used for molecular weight determination of cuprous oxide with fair success. However, an inverted example of such a calculation will perhaps appeal more to the metallurgist.

If E_a is the atomic freezing point lowering, t the lowering of the melting point, A the atomic weight of the solute, and m the number of grams of solute per 100 grams of solvent, the laws of perfect solution would require the expression

$$E_a = t\frac{A}{m}$$

for dilute solutions approaching the ideal. Suppose that this formula be used to calculate the composition of the eutectic. From the melting diagrams of Heyn[13] the eutectic melts at 1064°C., and pure copper at 1083,° whence t in the formula is $1083° - 1064° = 19°$. The value of E_a is 870.[14] Assuming the atomic unit of cuprous oxide in solution to be Cu_2O, A may be taken as $(2 \times 63.6 + 16) = 143.2$ Calculating m,

$$870 = 19\frac{143.2}{m}$$

$$m = 3.1$$

That is, on purely theoretical grounds, assuming that cuprous oxide in copper is an ideal solution, the composition should be 3.1 per cent. of Cu_2O. Heyn's data show an observed composition of 3.4 per cent., which must be considered an excellent agreement for this sort of calculation.

In view of the above considerations, which seem to show the normal nature of the solubility of cuprous oxide in copper, it would seem pertinent to ask the authors of this paper for further and more explicit justification for their colloid dispersion hypothesis. Although one must admit the possibility of such systems in metals, in this specific case rather direct and unequivocal data would seem required even to warrant consideration of such an idea.

W. H. OSBORN, New York, N. Y. (written discussion).—The premises on which the conclusions of this paper are based seem to us to be founded on an insufficient interpretation of the experimental data given:

1. In regard to the sulfur elimination from the deoxidized copper prepared by melting cathode in a graphite crucible in an atmosphere of hydrogen, we have found by repeated experiments that a current of pure, dry oxygen-free hydrogen acting on

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[13] E. Heyn: Untersuchungen über den Angriff des Eisens durch Wasser. *Mitt.* K. Tech. Versuchsanstalten (1900) 38.

[14] Landolt-Börnstein: Physikalisch-chemische Tabellen, 1, 54. Berlin, 1923. Springer.

completely deoxidized copper will remove sulfur from that copper at an excessively slow rate of speed. These experiments are confirmed by work by Jellinek[15] on the equilibrium system Cu-S-H showing very low vapor pressures of H_2S. Furthermore, analysis of the best Acheson graphite shows appreciable amounts of sulfur, which will contaminate copper melted in a crucible made from it. Copper made in the manner described, we have found by repeated experiments, will contain appreciable amounts of sulfur; probably in the neighborhood of 0.001 per cent.

2. In Table 1, series 1, CO_2 in the presence of carbon at temperatures over 1083°C. is almost completely converted to CO, hence substantially no CO_2 was present under the conditions of this series of runs.

3. In Table 1, series 2, CO_2, even if containing no traces of oxygen, is slightly oxidizing to copper, as is demonstrated by the work of C. G. Maier.[16] Furthermore, commercial bottled CO_2 contains traces of oxygen and unless especially deoxidized is highly oxidizing to copper. No carbon being present in the runs of this series, it is obvious that the copper melted under CO_2 was somewhat oxidized. As this copper also contained sulfur, there are no data given to prove conclusively that the porosity noted was due entirely to the CO_2 liberated and not, at least in part, to the reaction between the oxide and the sulfide to form SO_2.

4. In Table 1, series 3, oxygen-bearing copper melted in a graphite crucible is completely and rapidly deoxidized by its contact with carbon, as we have found in repeated experiments, the rate of deoxidation depending on factors of time, temperature and amount of agitation of the melt. Without further information on the exact technique of the runs of this series, the presumption would be that the high porosity shown with CO and H_2 was due to the fact that, because of the shorter time of the run, deoxidation was not yet complete and CO_2 in one case and H_2O and CO_2 in the other were still being evolved at the time of solidification.

5. Regarding density of copper melted under SO_2 and remelted *in vacuo* (Table 3), in our own experimentation we have melted and cooled deoxidized cathode copper in a current of SO_2 and obtained a product showing by analysis both O_2 and S present in approximately equal amounts, when the melt was cooled, which checks the microscopic findings made in this paper. This would indicate that it is possible for both oxygen and sulfur to be present in molten copper at the same time in equilibrium with an atmosphere of SO_2. By general chemical analogy, we feel justified in assuming that the lower the temperature of the bath, the less will be the concentration of O_2 and S, which will exist in equilibrium with SO_2. Hence, if copper is melted under SO_2 at any temperature above 1083°, and S and O_2 are thus introduced into the melt in equilibrium with SO_2 for that temperature, as the bath is cooled and temperature of solidification is reached, the concentration of S + O_2 will decrease and SO_2 will be liberated until equilibrium for the temperature of solidification (1083°) is reached. This formation of SO_2 in cooling would seem to account for the porosity of the first melt of Table 3. When remelting *in vacuo* the concentration of O_2 and S in the copper had already been reduced to a point where their reaction to form SO_2 at any temperature over 1083° was very slight and, as any SO_2 formed would be taken out of the equilibrium by the vacuum maintained, it is natural that the resulting product should be of high density and yet still show O_2 and S present.

To sum up, it appears to us that the premises on which the conclusions of this paper are based have not taken into consideration the chemistry of the reactions between the elements of the crucibles, the metal, and the gases used in the test runs

[15] K. Jellinek und J. Zakowski: Über die Affinität der Metalle zum Schwefel. *Ztsch. f. anorg. Chem.* (1925) **142**, 1.

[16] C. G. Maier: The Reduction of Cuprous Oxide by Carbon Monoxide. U. S. Bur. Mines *Repts. of Investigations* Serial No. 2926 (1929).

and that, if these reactions were more closely investigated, they would point to quite a different set of conclusions than those which were drawn from the experimental observations made.

O. W. ELLIS, Toronto, Ont.—The authors of this paper have presented for consideration the results of a series of tests on samples of copper melted under various conditions. The nature of these conditions is described so briefly as to make it almost impossible to visualize them. They state that the experiments "have been along the line of those performed by Lobley and Jepson," but leave to the imagination of the reader how far along this line they have proceeded. No idea of the weights of metal involved in the experiments can be obtained from their paper, nor is mention made of the rate of cooling of the metal subsequent to fusion and gasification. That densities of such a high order have been observed is also surprising. No analyses being quoted of the copper used in these experiments, it leaves the reader with food for thought as to possibilities of contamination of the copper used by something of higher density than copper itself.

That part of the paper most completely elaborated deals with the authors' theory of the colloidal dispersion of cuprous oxide in molten copper. The writer's thoughts on reading this section of the paper naturally reverted to certain suggestions he put forward in his paper on Gases in Casting Copper, referred to by the authors.[17] In commenting on the fact that the total gas content of a series of hypereutectic copper oxygen alloys varied directly as the amount of oxide in the ingots, the writer said, "It is possible, however, that the amount of oxide which separates from a melt during cooling may have an important effect upon the total quantity of gas (not necessarily upon the composition of the gaseous mixture) occluded by the solid metals. If the particles of oxide are considered as nuclei upon which gas may be adsorbed, then the fact that ingot 13 (about 0.068 per cent. O_2) contains more gas than either ingots 14 (about 0.61 per cent. O_2) or 15 (about 0.32 per cent. O_2) may be explained on the assumption that the amount of oxide upon which gas could be adsorbed was greatest in the case of the first casting."

Here the writer was treating of hypereutectic alloys, alloys in which copper oxide separated from the melt at the liquidus with consequent enrichment of the liquid phase in copper. To have applied these remarks to alloys in which copper separated from the melt at the liquidus with consequent enrichment of the liquid phase in oxygen would, to the writer's mind, have been impossible, in view of the fact that copper oxide as a separate entity would not exist until the liquid had become of eutectic composition.

The authors of this paper, however, have discarded what "metallographists have usually assumed" with, it is thought, abundant good reason, and have introduced a theory which apparently is in direct opposition to all those laws of equilibrium upon which, for example, the phase rule is based.

In support of their theory they quote the case of the "modification" of the alloys of aluminum and silicon by sodium, overlooking the well-established facts (1) that "modification" of these alloys under certain conditions of cooling can be effected without the aid of sodium and (2) that curves of solubility for these alloys modified by sodium correspond so closely to the supersolubility curves of the normal alloys as to make it next to impossible to doubt that all that sodium does is, as Miss Gayler [18] has said, to cause "crystallization" in the modified alloys "to take place at the temperature of spontaneous crystallization."

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[17] O. W. Ellis. *Op. cit.*, 460.

[18] M. L. V. Gayler: The Under-Cooling of Some Aluminum Alloys. *Jnl.* Inst. Metals (1927) **38**, 157.

To employ so remarkable a proof as this of the genuineness of our present conceptions of equilibrium conditions in solutions to support a theory of colloidal dispersion is going rather far! And to suggest that "with this evidence of a coarse colloidal condition in what was thought to be a molecular solution, there can be little hesitancy in assuming cuprous oxide to be colloidally dispersed in molten copper" is going so far and so fast that I fear few of us will be able to follow.

H. M. St. John, Detroit, Mich.—Mr. Barker's reference threatens to introduce a point that should be discussed under other papers.[19] Referring to the paper given by Bolton and Weigand last year, with respect to the comparative effect of carbon monoxide and carbon dioxide on brass and bronze, I think we can say by general consent that it is unsafe to make any direct comparision between the effect of these gases on pure copper and on brass or bronze.

R. C. Dalzell.—This paper was written with the principal object of presenting a new theory. The theory was simply suggested by the laboratory work, and we had no expectation that it would stand on the basis of such meager data. We felt that the real test would be its applicability to the phenomena observed in practice. The discussion from this angle has been very friendly to the theory and calls for no reply.

Several objections to the laboratory work must be answered.

1. We were aware of the fact that moist hydrogen is much more effective than the dry gas in removing sulfur. Accordingly, water vapor was always mixed with the hydrogen used for this purpose, the gaseous mixture being approximately 10 per cent. H_2O by volume. Later, however, when testing the effect of hydrogen on the porosity of both oxidized and deoxidized copper, the gas was dried on its way to the furnace tube.

2. We relied, perhaps unwarrantedly, on the lead acetate test to indicate that all of the sulfur had been removed from the copper and the graphite.

3. The reaction $CO_2 + C \rightarrow 2CO$ requires an active form of carbon for rapid completion. Graphite does not approach this requirement.

4. The CO_2 was passed through red-hot copper gauze to remove O_2.

5. Generally speaking, dilute inorganic solutions react practically instantaneously. Hence it seems to us that Mr. Osborn's fifth point is not well taken.

6. Replying to Mr. Ellis: All melts were made in a closed-end vitreosil furnace tube in an atmosphere consisting solely of the gas under observation. A high-frequency induction furnace was used for heating.

Ingots made in the graphite crucibles weighed approximately 3 lb. each; those made in vitreosil crucibles weighed about 1 lb. The copper used is known as re-electrolyzed series cathodes. High-grade cathodes from the series refinery at Baltimore were put in bags and used as anodes in electrolyzing a solution of pure acid and copper sulfate. The resulting cathodes were cut in small pieces and carefully cleaned prior to use in these experiments. There is no possibility that the metal was contaminated with metals of higher density.

We suggest, as an aid to seeing our viewpoint, the reading of the chapter by H. W. Gillett in Bogue's "Colloidal Behavior."[20] This chapter is a most interesting discussion of colloidal phenomena in metals and alloys.

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[19] See papers beginning on pages 316, and 368.
[20] McGraw Hill Book Co., New York, 1924.

Effects of Oxidation and Certain Impurities in Bronze

By J. W. Bolton* and S. A. Weigand,† Cincinnati, Ohio

This paper discusses some fundamental metallurgical principles involved in production of sound cast bronze. In a previous paper the writers advanced the theory that "oxidation" in bronze castings is due to incipient shrinkage, and showed the effect of reducing melting atmospheres.[1] In the present paper the effects of certain impurities and of actual oxidizing conditions are shown. The appendix deals with the appearance of various inclusions.

For many years the prevailing opinion has been that unsoundness, dark colored fractures and other phenomena accompanying porosity and weakness in bronzes are due to oxidation. The actual troubles are caused by fissures of intercrystalline type, which are often mistaken for intercrystalline films. These weaken the metal and make it porous. Grave doubt regarding the accuracy of the oxidation theory appears when several research papers presented within the last 10 years are reviewed critically.

In 1919, Comstock[2] conducted metallographic researches, attempting to identify "oxides" in synthetically prepared metals. He found that oxides of tin, aluminum, zinc, etc. are different from the intercrystalline films (or cavities) to which porosity is due. Apparently he believed that these "oxide films" may be caused by volatile oxides of zinc or of phosphorus or by dissolved gases thrown out of solution during solidification of the metal.

In 1923, Woyski and Boeck[3] definitely questioned the accuracy of the oxidation theory and indicated the danger from reducing atmospheres. They say that "oxidation, gassing and shrinkage may produce effects very similar."

In 1926, investigations by Iwasé[4] showed marked change in absorption coefficients for various gases in copper above and below the liquidus.

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[1] J. W. Bolton and S. A. Weigand: Incipient Shrinkage in Some Non-Ferrous Alloys. *Trans.* A. I. M. E. (1929) Inst. Met. Div., 475.

[2] G. F. Comstock: Non-metallic Inclusions in Brass and Bronze. *Trans.* A. I. M. E. (1919) **60**, 386.

[3] B. Woyski and J. W. Boeck: Gas Absorption and Oxidation of Non-ferrous Metals. *Trans.* A. I. M. E. (1923) **68**, 861.

[4] K. Iwasé: Occlusion of Gases by Metals and Alloys in Liquid and Solid States. *Sci. Repts.* Tohoku Imp. Univ. [1] (1926) **15**, 531.

Cowan[5] showed, in 1927, that minute shrinkage cavities in certain heterogeneous alloys are due to shrinkage accompanying the change in volume, between liquid and solid phases, of a component of relatively low freezing point where it last freezes after the bulk of the alloy has solidified at higher temperature.

O. W. Ellis[6] stated that copper melted under reducing conditions (in the indirect-arc furnace) contains principally carbon dioxide, nitrogen, and water vapor; hydrogen and carbon monoxide being absent. To the writers of this paper it seems that it may be possible that under certain conditions oxygen (air) might unite with possible CO and H in the metal with formation of the products mentioned.

In the previous paper the authors showed that unsoundness is due to intercrystalline fissures rather than to films.[7] These fissures are caused by rather general incipient shrinkage, differing in degree only from ordinary foundry shrinkage cavities. This condition is pronounced in some zinc bronzes melted under highly reducing atmospheres, and in cases where the "feeding" of the sections is poor. This latter condition is traceable to gating practice, pouring temperature, or any conditions affecting the flow or viscosity of the metal. In general, their work confirms that of Woyski and Boeck regarding the influence of atmospheres and gating.

H. C. Dews[8] claims that porosity is due to the long freezing range of cast bronze and its contraction in volume during freezing. Further, "even when a supply of metal is available, it has to flow through a maze of (already formed) dendrites to fill up the spaces."[9] "Small amounts of phosphorus lengthen the freezing range, hence tendency toward unsoundness—there is plenty of evidence that an oxidizing atmosphere is essential to produce good quality bronze." One foundryman found that when melting "under reducing conditions the addition of lead oxide was necessary to induce soundness."

CONCLUSIONS FROM EARLIER WORK

These reviews, while by no means exhausting the literature, afford sufficient experimental data to justify the following conclusions:

1. Ordinary porosity in cast bronze is due to intercrystalline fissures, not films.

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[5] W. A. Cowan: Synopsis of paper on Minute Shrinkage Cavities in Some Cast Alloys of Heterogeneous Structure. *Jnl.* Inst. Metals (1927) **38**, 4.

[6] O. W. Ellis: Absorbability of Gases in Casting Copper and Effect of Adding Cuprosilicon. *Trans.* A. I. M. E., Inst. of Met. Div. (1929) 443.

[7] J. W. Bolton and S. A. Weigand: *Op. cit.*

[8] H. C. Dews: Practical Points from the Metallurgy of Cast Bronzes. Inst. Brit. Foundrymen *Paper No.* 8, presented at International Foundry Congress, 1929.

[9] This assumes (1) vacuum or reduced pressure spaces or (2) presence of gases which must be displaced or reabsorbed.

a. This is shown by the microscope. In many cases the change from actual (macroscopic) drawholes or localized shrinkage cavities to inter-crystalline fissures or general incipient shrinkage is one of degree and distribution only.

b. True oxides appear as inclusions, which generally have little resemblance to the fissures or alleged films.

c. The coloration of fracture associated with "oxidation" is an incidental phenomenon. Porous metal may appear "clear" on a fresh fracture, the water or gases during test or manufacture discolors the exposed facets.

d. The effects of incipient shrinkage usually occur in the sections of the casting last to solidify, and in the beta-rich phase.

2. This condition (incipient shrinkage) is common in metals melted under reducing atmospheres, particularly those in CO. Boeck[10] mentions burning these rejected gases. The condition has been minimized by

a. Melting with neutral (CO_2) atmospheres;

b. Addition of easily reduceable oxides such as those of lead and copper.

3. The condition is manifested by lowered strength and elongation, and decrease in specific gravity (Fig. 23) in the alloy 88-6-4-2.

4. Incipient shrinkage also is influenced by the following factors:

a. General contraction characteristics of the specific alloy and its length of freezing range.

b. Difference in volume contraction of components in heterogeneous type alloys.

c. Fluidity of the alloy at various temperatures.

d. Pouring temperature of alloy.

e. Design of casting.

f. Cooling rate of casting.

g. Foundry provision for feeding casting.

h. Condition of atmosphere other than reducing or neutral (*i.e.*, oxidizing).

i. Presence of impurities and minor amounts of certain elements.

EFFECT OF OXIDATION

A heat of virgin metal was melted and poured into ingot. This showed the following:

	PER CENT.		
Copper....	87.14	Tensile strength, lb. per sq. in.	41,750
Tin........	5.72	Elongation, per cent..	44.4
Zinc...	4.87	Elastic limit	17,500
Lead.	2.07		

[10] J. W. Boeck: Discussion of paper by Bolton and Weigand. *Trans.* A. I. M. E., Inst. Met. Div. (1929) 492.
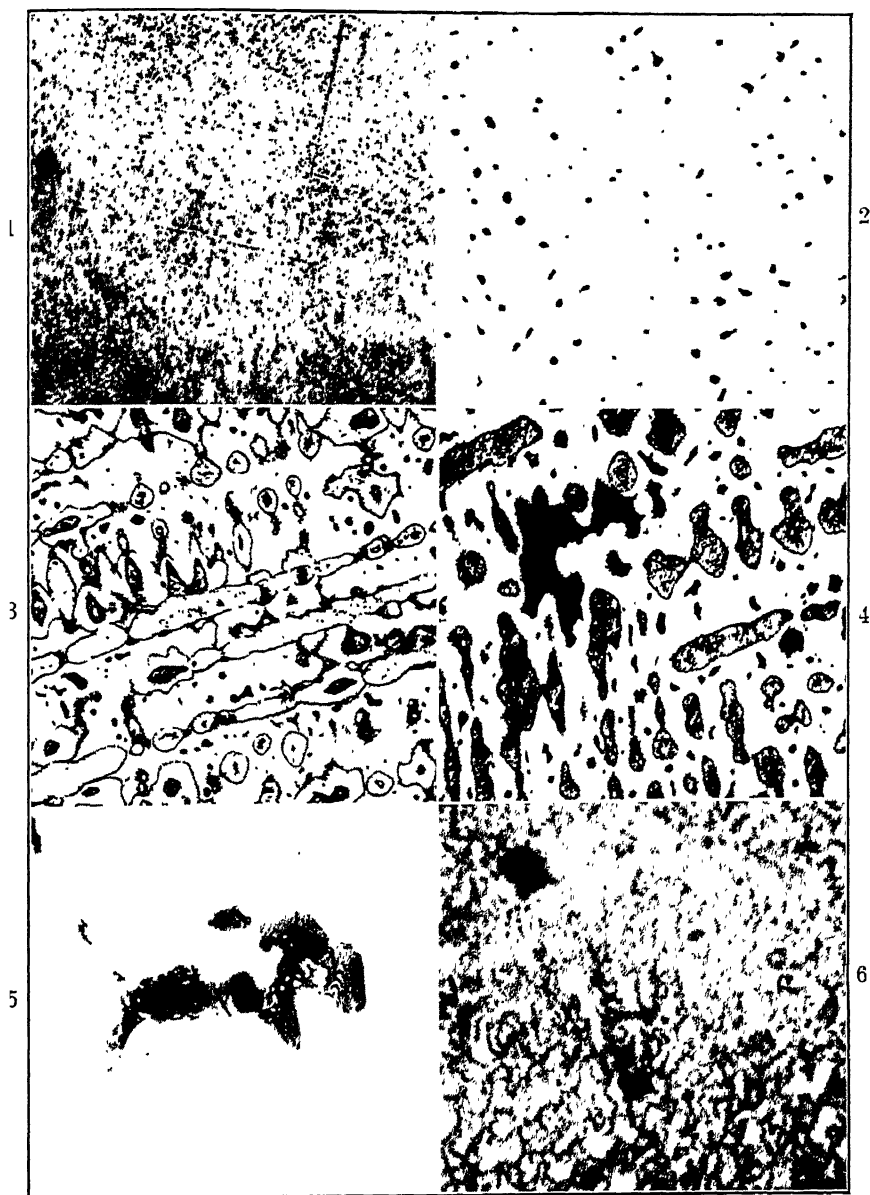
FIG. 1.—LEAD-FREE AREA OF BETA-RICH BRONZE. × 1000. LIGHT ETCH WITH H_2O_2.
FIG. 2.—LEAD DISTRIBUTION. × 100.
FIG. 3.—TWICE REMELTED METAL OF FIGS. 1 AND 2 IN OXIDIZING ATMOSPHERE.
ETCHED WITH H_2O_2. × 100.
FIG. 4.—SAME AS FIG. 3.
FIG. 5.—TYPICAL INCLUSIONS. × 1000.
FIG. 6.—PECULIAR ETCHING EFFECT. × 2000. LIGHT ETCH WITH H_2O_2.

A typical photomicrograph of lightly etched section of this alloy in the beta-rich phase is shown in Fig. 1, lead-free area. General appearance showing lead distribution is shown Fig. 2; pouring temperature, 2200° F.

This metal was remelted twice in an oxidizing atmosphere; pouring temperature, 2180° F. Results are—

PER CENT.

Copper.....	90.48	Sulfur, per cent......	0.033
Tin.....	5.78	Tensile strength, lb. per sq. in.	32,145
Zinc..	1.33		
Lead	2 21		

Metal was poor and showed some brown-red spots like those in gassed bronze. Photomicrographs are shown in Figs. 3 and 4, both etched. The metal was very sluggish. Typical inclusions are shown in Fig. 5 and a peculiar etching effect is revealed in Fig. 6.

EFFECT OF SILICON

In the previous paper mentioned, the writers showed that the bronze studied at that time was substantially free from silicon, containing only about 0.006 per cent. Silicon was added up to 0.03 per cent. No changes in the characteristics of the alloy were noted. Then the effect of 0.07 per cent. silicon in the finished alloy was examined. In spite of slight porosity, as shown in Fig. 7, the physical properties are as shown in Table 1. The fracture looked good, although tendency toward dendritism was negligible. The outside of the casting had a distinct silver-like tinge.

TABLE 1.—*Effect of Silicon in Bronze*

Amount of Silicon, Per Cent	Tensile Strength, Lb. per Sq In.	Elongation in 2 In , Per Cent.	Elastic Limit, Lb. per Sq. In.	Pouring Temperature, Deg. F.
0 07	42,410	40.4	17,750	2180
	43,370	53.3	17,180	
0.29	38,810	20.0	19,500	2200
	38,450	19.3	19,550	

With 0.29 per cent. silicon in finished alloy the physical properties were as shown in Table 1. The drop in elongation is pronounced. Elongation is much lower than that obtained in the regular alloy. Brinell hardness is 74, which is high for this alloy. Microstructures are shown in Figs. 8, etched, and 9, unetched.

The fracture was close grained on the edge but was lemon yellow and open grained in the center of the section. Pouring temperature was 2200° F. and the metal poured clear and fluid. The exteriors of the castings were covered with thin white films and there was com-

plete absence of bronze color. Tops of risers were blackened and smooth appearing.

Higher magnification shows no inclusions or new components that might be considered typical and due to silicon. Silicon evidently goes into solid solution in the alloy. The writers believe that it exerts a dele-terious effect by changing either the contractive or fluidity properties or both. In larger percentages it raises the elastic limit and maintains
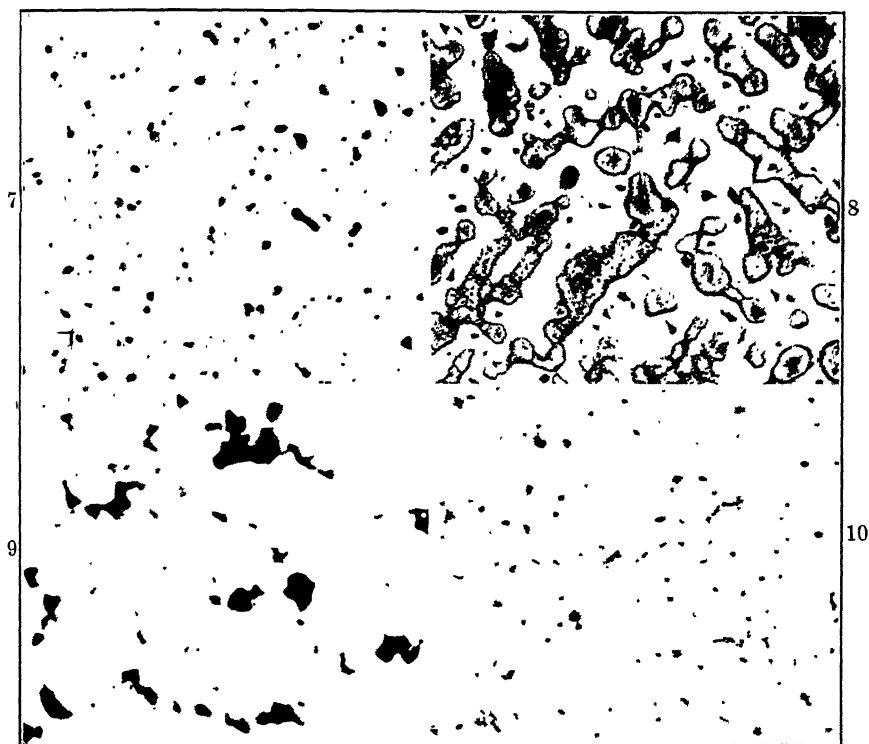
FIG. 7.—BRONZE CONTAINING 0.07 SILICON, × 100. ETCHED WITH H₂O₂.
FIG. 8.—BRONZE CONTAINING 0.29 PER CENT. SILICON, × 100. ETCHED WITH H₂O₂.
FIG. 9.—SAME AS FIG. 8, UNETCHED.
FIG. 10.—BRONZE CONTAINING 0.068 PER CENT. SULFUR, × 100. UNETCHED.

tensile strength even though the center of the bar is very porous. In the writers' opinions 0.05 per cent. silicon or over is likely to prove dangerous in plant practice.

EFFECT OF SULFUR

Additions of lump sulfur were made to experimental heats. As in all the work referred to herein the percentages of impurity reported is that determined by analysis in the finished alloy.

With sufficient sulfur to produce 0.046 per cent. sulfur in the finished alloy, physical properties were as shown in Table 3. Behavior of metal in handling and appearance in castings was like regular bronze. Fracture was fair. Analysis is too high in zinc (Table 2).

TABLE 2.—*Complete Analysis Log*

Impurity		Cu Per Cent	Sn Per Cent.	Zn Per Cent.	Pb Per Cent.	Brinell Number
Kind	Per Cent.					
Si.............	0.07	87.98	6.09	3.60	2.06	65
Si...	0.29	86.40	6.37	4.79	1.90	74 (high)
S.....	0.046	87.20	5.67	5.03	1.87	65
S....	0 068	88.42	6.08	3 19	2.04	61
S....	0.140	87.48	5 83	4.79	1.56	62
S.....	0.231	88 38	5.67	3.58	1.94	63
Al...	0 05	88.04	6.28	3 32	2.11	61
Al............	0.13	86 94	5 97	4.79	1 97	57 (low)

With 0.068 per cent. sulfur physical properties were as shown in Table 3. Fracture was fair, with a tendency toward looseness. With this percentage of sulfur the castings had a greenish tinge on the skin, although no peculiarities were noted in the molten metal. As shown in Fig. 10 (unetched) a third component shows up faintly on the polished sample, among the darker spots due to lead and porosity.

With 0.14 per cent. sulfur physical properties were as shown in Table 3. The molten metal appeared to be slightly sluggish. The castings

TABLE 3.—*Effect of Sulfur in Bronze*

Amount of Sulfur, Per Cent.	Tensile Strength, Lb per Sq. In.	Elongation in 2 In , Per Cent.	Elastic Limit, Lb. per Sq. In.	Pouring Temperature, Deg. F.
0.046	35,000	24 8	16,300	2200
	35,410	25 6	16,600	
0.068	38,140	31 9	16,440	2180
	36,820	28 0	16,420	
0.14	38,600	34.7	16,970	2150
	39,430	38.1	16,590	
0 231	37,660	26 0	16,810	2150
	36,010	28 0	16,590	

had a faint tendency toward greenish tinge. Fractures of test bars appeared good. The machined and pulled bars had a peculiar appear-

ance. As on any ductile alloy, stretching caused the ribbed grain appear-
ance; on these bars one side showed small grains, the other showed coarse
grains (Figs. 11 and 12).

At this percentage (0.145 per cent.) the photomicrograph (Fig. 13)
shows peculiar structure, a symmetrical and unidirectional orientation
of dendrites. Fig. 14 shows a typical inclusion, magnified 1000 dia.
Color of inclusions were blue gray or slate color.
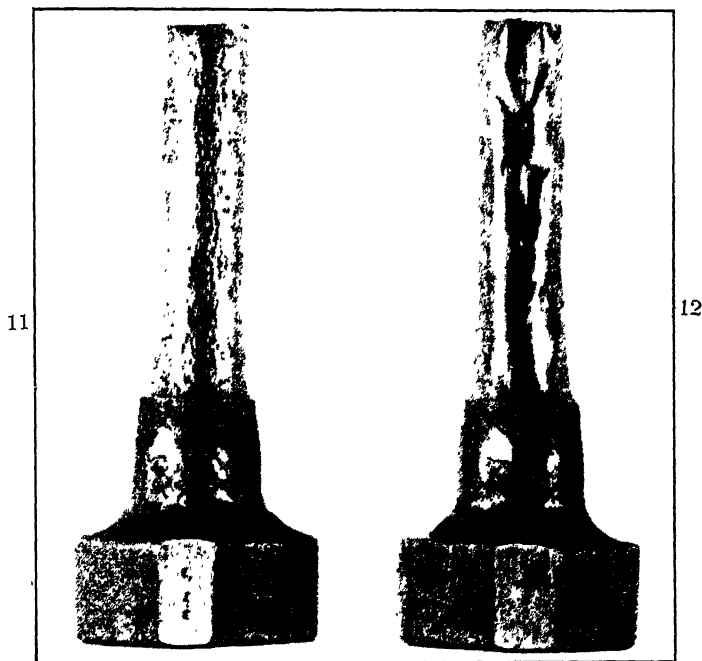
FIGS. 11 AND 12.—SAME MACHINED AND PULLED BARS CONTAINING 0.14 PER CENT.
SULFUR, SHOWING COARSE AND FIND-GRAINED SIDES.

When the sulfur was increased to 0.231 per cent. the physical proper-
ties were as shown in Table 3.   No peculiarities were noted in the molten
metal.   Fractures were fair and castings had a decidedly greenish tinge.
Photomicrograph at 100 dia., etched, is shown in Fig. 15 and shows no
highly unusual features.   At 100 dia., unetched, the center shows some-
what porous (Fig. 16).   There is a slight tendency for the inclusions to
form broken networks, as shown in Fig. 17.   Etching shows local pitting
near such formations.   Typical inclusions are shown in Fig. 18.   Nearly
all of these occur in the beta-rich portions.

According to these tests the effects of sulfur are not marked, but it
seems dubious practice to maintain this impurity over 0.05 per cent. if
best results are desired.

FIG. 13.—BRONZE CONTAINING 0.140 PER CENT. SULFUR.   × 100.   ETCHED WITH H₂O₂.

FIG. 14.—TYPICAL INCLUSION IN 0.14 PER CENT. SULFUR.   × 1000.   UNETCHED.

FIG. 15.—BRONZE CONTAINING 0.231 PER CENT. SULFUR.   × 100.   ETCHED WITH H₂O₂.

FIG. 16.—CENTER OF BAR SHOWN IN FIG. 15.   × 100.   UNETCHED.

FIG. 17.—NETWORK OF INCLUSIONS IN BRONZE OF FIG. 15.   × 1000.   SLIGHT ETCH WITH H₂O₂.

FIG. 18.—TYPICAL INCLUSIONS OF BRONZE CONTAINING 0.231 PER CENT. SULFUR × 1000.   UNETCHED.

EFFECT OF ALUMINUM

Aluminum, on the other hand, has a bad influence, and a small amount of it is dangerous.

With 0.050 per cent. aluminum, physical properties are as shown in Table 4. The fracture exhibited tan spots, dispersed rather than only

TABLE 4.—*Effect of Aluminum in Bronze*

Amount of Aluminum, Per Cent.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Elastic Limit, Lb. per Sq. In.	Pouring Temperature, Deg. F.
0.050	38,200	27.7	17,460	2180
	39,600		17,560	
0.13	31,500	20 9	16,160	2200
	30,640	21.1	16,040	
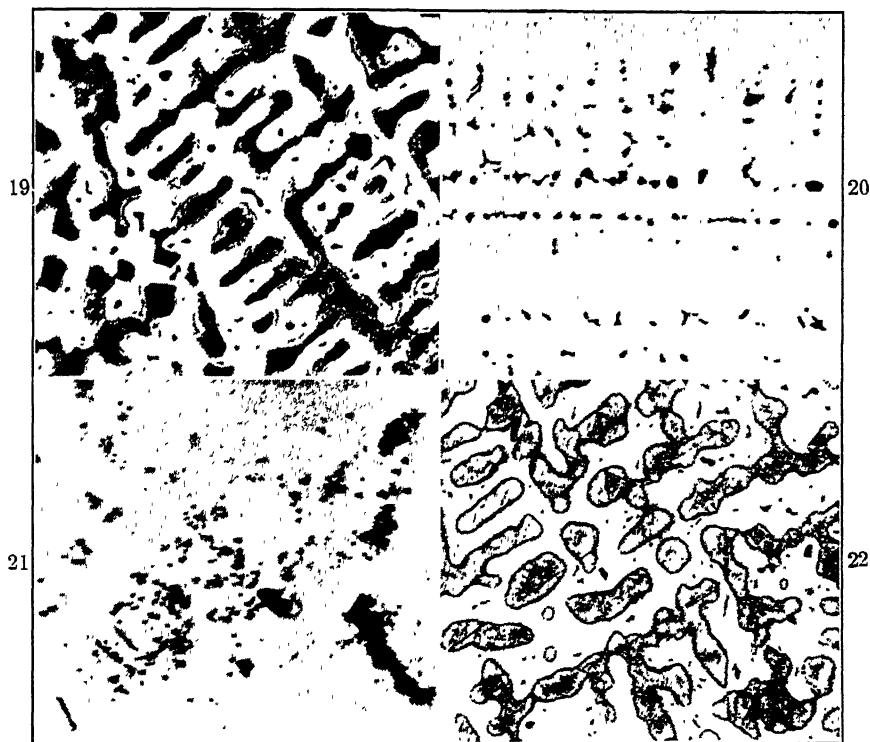
FIG. 19.—BRONZE CONTAINING 0.050 PER CENT. ALUMINUM. ✕ 100. SLIGHTLY OVERETCHED WITH H_2O_2.
FIG. 20.—SAME AS FIG. 19. ✕ 100. UNETCHED.
FIG. 21.—TYPICAL ALUMINA INCLUSIONS IN BRONZE CONTAINING 0.13 PER CENT. ALUMINUM. ✕ 1000. SLIGHTLY ETCHED WITH H_2O_2.
FIG. 22.—SAME AS FIG. 21. ✕ 100. ETCHED WITH H_2O_2.

at the center, as sometimes is found in regular alloys. Castings had silvery appearance; shrinkage in sprue was normal. As shown in Figs. 19 (slightly overetched) and 20 (unetched), there is tendency toward dendritism and large grain size. This also shows on the side of the machined and pulled tensile bar.

When the alloy contained 0.13 per cent. aluminum properties were as shown in Table 4. The fracture exhibited a coarse and dendritic structure and had largely a tan-yellow color. Skin of castings was white and looked somewhat like aluminum bronze. Sprues had smooth top
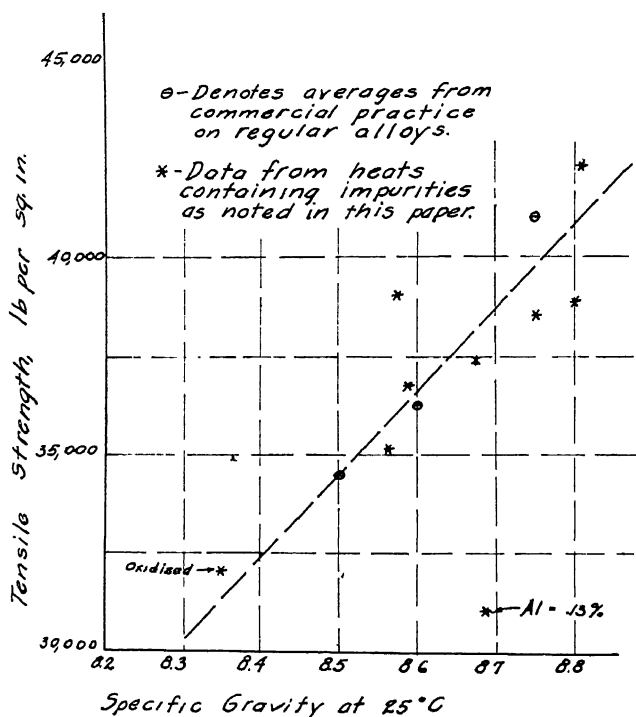
FIG. 23.—RELATION OF STRENGTH AND SPECIFIC GRAVITY.
Determined on samples containing various impurities and others low in impurities made in commercial practice.

like manganese bronze. Typical alumina inclusions are seen at higher magnifications (Fig. 21). Structure of etched alloy at 100 dia. is shown in Fig. 22. Aluminum has a decided influence on the crystal structure and external (skin) appearance of the alloy. This is apparent at 0.05 per cent. or under.

CONCLUSIONS

Porosity due to incipient shrinkage is influenced by the furnace atmospheres. The bad influences of actual oxidation are apparent in incipient shrinkage, lowered strength, sluggishness of metal and

FIG. 24.—GASSED NAVY G. METAL. × 100. ETCHED WITH NH₃ AND H₂O₂.
FIG. 25.—UNSOUND PORTION OF METAL OF FIG. 24. × 500.
FIG. 26.—GASSED MONEL METAL. × 100. ETCHED WITH NITRIC-ACETIC ACID.
FIG. 27.—SOUND MONEL METAL. × 100. ETCHED WITH NITRIC-ACETIC ACID.
FIG. 28.—85–5–5–5 ALLOY. × 100. ETCHED WITH H₂O₂.
FIG. 29.—OXIDIZED BRONZE. × 100. ETCHED WITH CONC. HNO₃.

zinc loss. These remarks apply to metals containing only traces of impurities.

When melted in a crucible under practically neutral furnace atmospheres, the impurities silicon, sulfur and aluminum have effects which do not resemble the usual atmospheric effects. In some cases these impurities have a deleterious influence. Even small percentages of aluminum change the (skin) color of the alloy, and modify its crystallization characteristics. Larger percentages make it weak and brittle, with extremely coarse grain. The inclusions are incidental, if interesting. The hardness is reduced to 57, from 60 to 65. As shown in Fig. 23, the effect is not accompanied by as low specific gravity as is encountered in gassed metal.

Silicon also appears to go into solid solution and modifies the crystallization characteristics of the metal. When melted under neutral atmospheres, no inclusions attributable to presence of silicon are discernible. While silicon in minute amounts is not dangerous, over 0.05 per cent. should be avoided in commercial practice. In alloys high in lead this element may need to be held even lower.

The action of sulfur is less marked, but in the writers' opinions percentages over 0.05 per cent. are not desirable.

APPENDIX

In addition to the photomicrographs given in the body of this paper, Figs. 24 to 36 are of interest for comparison.

The gassed Navy "G" metal of Fig. 24 was etched with ammonia and hydrogen peroxide. The metal was melted in a reducing atmosphere. Fig. 25 shows an unsound portion of the same sample.

Fig. 26 is gassed monel metal, etched with nitric-acetic acid. The metal was melted in an atmosphere containing an excess of carbon monoxide. Fig. 27 is sound monel metal, melted in a neutral atmosphere. It was etched with nitric-acetic acid.

Fig. 28 represents 85-5-5-5 alloy, of 35,000 lb. tensile strength, melted in a neutral atmosphere. Note the freedom from intercrystalline fissures. The sample was etched electrolytically with hydrogen peroxide.

Fig. 29 is oxidized bronze, showing cavities and intercrystalline fissures, etched with concentrated nitric acid. Fig. 30 shows cavities at a higher magnification, lightly etched electrolytically with hydrogen peroxide. When high in tin the characteristic brilliant light blue, hard delta eutectoid is found, but in the composition studied the delta eutectoid and the phosphide areas of similar appearance are rarely found. Most inclusions are complex in nature. Lead shows as dull portions containing lighter spots or network. There is a dull light blue structureless component, slightly harder than the matrix, which is particularly
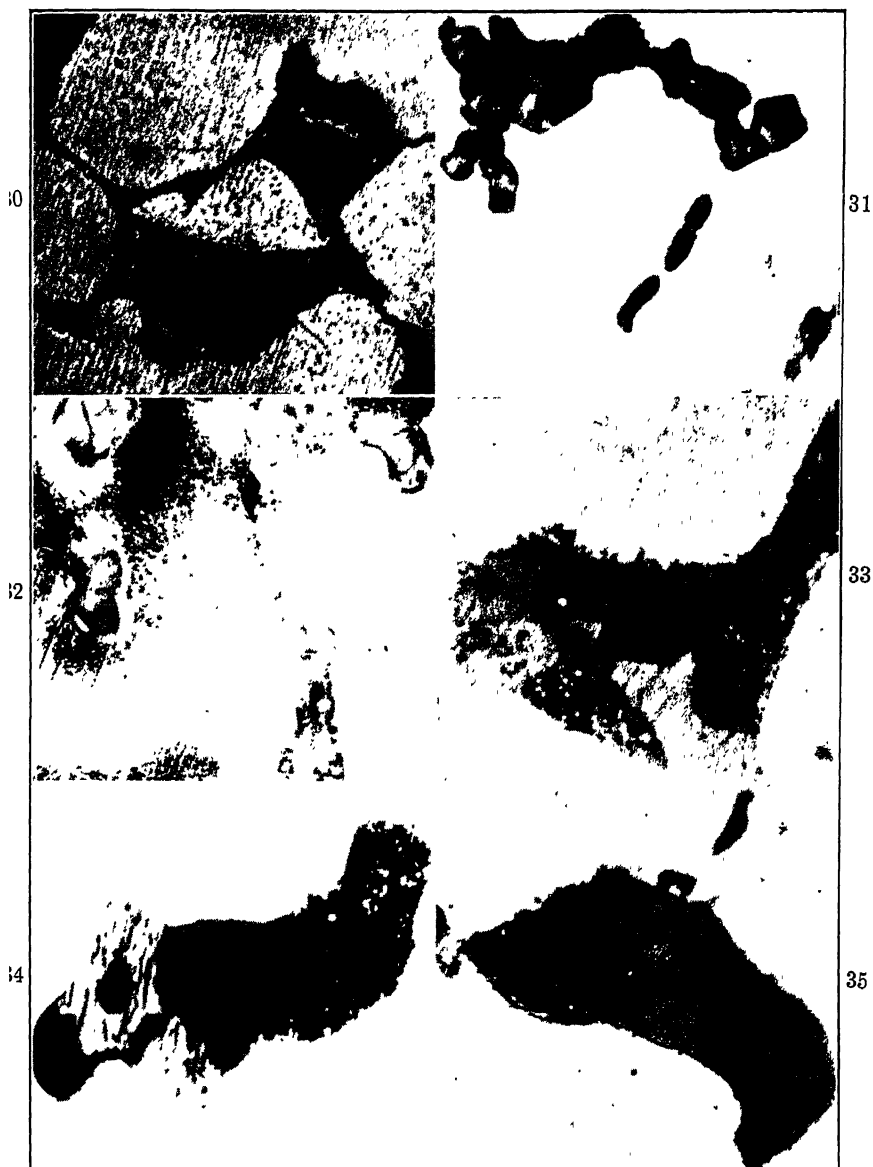
FIG. 30.—CAVITIES IN OXIDIZED BRONZE. × 2000. LIGHT ETCH WITH H$_2$O$_2$.
FIG. 31.—SUPPOSED SULFIDE INCLUSIONS IN BRONZE CONTAINING 0.231 PER CENT. SULFUR. × 1000. UNETCHED.
FIG. 32.—SAME SAMPLE AS FIG. 31. × 1000. ETCED WITH CONC. HNO$_3$.
FIG. 33.—SAME SAMPLE SHOWING INCLUSIONS EMBEDDED IN A GLOBULE OF LEAD. × 2000. UNETCHED.
FIG. 34.—SAME SAMPLE AS FIG. 31. × 2000. UNETCHED.
Lead at right. Black center probably a cavity out of focus.
FIG. 35.—SAME SAMPLE AS FIG. 34. LEAD UNDER RIGHT INCLUSION.

frequent in oxidized metal. No other allotriomorphic forms were found. Another characteristic formation (possibly two formations) is darker slate blue, somewhat softer than that mentioned above. Some of the slate blue components apparently have a tendency toward idiomorphic crystallization. All of the inclusions mentioned are more clearly shown when the sample is lightly etched. Supposedly sulfide inclusions in the sample containing 0.23 per cent. sulfur are shown in Fig. 31. These inclusions are unattacked by concentrated nitric acid, as shown in Fig. 32.
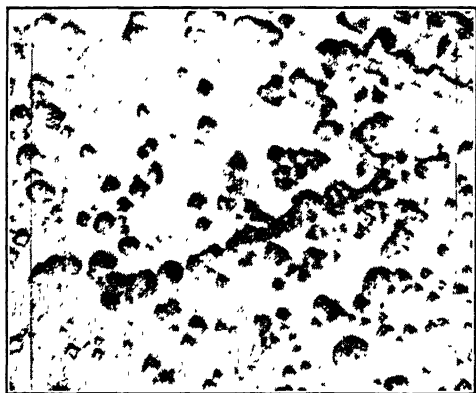
FIG. 36.—CUBICAL PITS FROM ETCHING IN CONCENTRATED HNO₃.   × 1000.

Complex inclusions found in oxidized bronze are seen in Figs. 33, 34 and 35. Most of the inclusions seem to be embedded in the lead, where they probably migrated or became entrapped during solidification. In Fig. 33 the inclusions are imbedded in a globule of lead. In Fig. 34 the lead is at the right and the black center is probably a cavity out of focus. In Fig. 35 the lead appears under the right inclusion. All these light and slate blue inclusions are attacked by concentrated nitric acid. It may be that they are zinc oxide and tin oxide solutions, respectively, or they may be more complex solutions of oxides, sulfides and silicates.

As a matter of interest to metallographists Fig. 36 is included. This shows cubical etching pits from concentrated nitric acid etching.

DISCUSSION

H. W. MAACK, Chicago, Ill. (written discussion).—The kind of melting furnace used in Bolton and Weigand's experiments is not made clear, although in their conclusion the authors mention crucible melting. Presumably suitable precautions were taken to eliminate such variables as contamination by the melting vessel.

In our own tests with silicon, 85–5–5–5 alloy was melted in crucibles in anthracite-fired furnaces, half of the melt poured into castings, silicon copper added and the remainder poured into duplicate molds of castings. With 0.047 per cent. silicon

(by final analysis), the castings had a green-gray colored surface, came clean from the sand and had a slightly gray, segregated fracture. These results confirm those of the authors as to effect of silicon and the maximum safe content in leaded red brass, also those of H. M. St. John.[11]

Sulfur in bronze, in our experience, may not be as harmful as it has been reputed to be. Under the microscope in our tests it appeared as dark blue-gray globules, presumably copper sulfide, similar to manganese sulfide in steel. These seemed to have a tendency to rise to the top of the small ingots poured. Castings had a dark brown skin but fractures were not always affected. However, with 0.50 per cent. sulfur, the fracture was decidedly abnormal.

Mr. Bolton found amounts over 0.50 per cent. undesirable. We are inclined to think this a rather low figure. Composition ingots of 85–5–5–5 formula from five different refiners analyzed from 0.09 to 0.24 per cent. sulfur, most of them having about 0.10 per cent. The regular run of castings of similar composition, in which like ingots were a part of the charge, showed 0.05 to 0.10 per cent. sulfur and were normal pressure tight castings in every respect. However, furnace atmosphere may have much to do with the manner in which sulfur in bronze shows its presence.

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[11] See page 384.

The Influence of Silicon in Foundry Red Brasses

By H. M. St. John,* G. K. Eggleston† and T. Rynalski,† Detroit, Mich.

Maintaining a satisfactory structure in brass and bronze castings has always been a foundry problem of great practical importance. While metallurgists and scientific investigators have not entirely ignored this matter, it has received less of their attention than has been given to iron, steel and the wrought copper and aluminum alloys. Investigation in this field has probably been discouraged to some extent by the complicated nature of the alloys involved. Hundreds of alloys are in more or less common use, most of them containing copper, zinc, lead and tin in widely varying proportions. They also contain appreciable percentages of iron and antimony as impurities, and often phosphorus, which has been added as a deoxidizer and fluidifier. Small amounts of sulfur are usually present. It is not uncommon to find nickel, sometimes in rather substantial quantities. Traces of other metals are frequently present. So complicated and variable a mixture obviously offers difficulties in any investigation of the various factors that influence the structure and other properties of the casting.

Incipient Shrinkage

Bolton and Weigand[1] have called attention to a type of structure characterized by intercrystalline fissures and large dendritic crystals which are frequently tarnished to an orange or reddish brown color. This intercrystalline porosity they term "incipient shrinkage" and attribute to the presence of carbon monoxide in the atmosphere under which the metal was melted.

The defective structure to which Bolton and Weigand refer has become a brass-foundry problem of major importance, because it occurs with distressing frequency in leaded brasses and bronzes when these are melted in a neutral or reducing atmosphere. Since the electric furnaces, now coming into general use in brass foundries, normally operate with such an atmosphere and, in fact, depend upon it in part

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[1] J. W. Bolton and S. A. Weigand: Incipient Shrinkage in Some Non-ferrous Alloys. *Trans.* A. I. M. E., Inst. Metals Div. (1929) 475.

for the remarkably low oxidation and volatilization loss which is one of their principal advantages, it is increasingly important to determine whether this reducing atmosphere is in itself a disadvantage in its effect on metal quality. While it is possible to eliminate or at least minimize the difficulty by operating the electric furnace with an atmosphere that has deliberately been made oxidizing in character, it is apparent that this cannot be done without, to some extent, sacrificing the inherent advantage peculiar to electric-furnace melting. If the trouble were due to direct action of carbon monoxide on the metal it would be necessary to make such a compromise but if this is not the case a solution of the problem that will leave the reducing atmosphere of the furnace undisturbed is to be preferred.

Just 10 years ago one of the authors of this paper had his first experience with an epidemic of bad castings from a leaded foundry brass melted in a rocking electric furnace. The structure of the metal was very bad—large dendritic crystals with wide spaces between them, the lead segregated, partly on the surface of the castings, partly in the space between the crystals. The surface of the castings had a worm-eaten appearance, the pits of which were filled with zinc oxide, the smooth portions of the surface often covered with a silvery film of lead. It looked much like an aluminum contamination but no aluminum could be found. The metal was so weak that most of the castings broke when an attempt was made to machine them while those which could be machined proved to be very porous and leaky when put on a hydraulic test.

In this case it was found that the difficulty originated with oil carried by screw-machine turnings which formed part of the furnace charge. In the reducing atmosphere of the electric furnace this oil suffered a destructive distillation and the metal poured from the furnace was covered thickly with finely divided carbon. As soon as the oil was eliminated the trouble disappeared and metal of normal quality was produced without difficulty.

It has since been found that any considerable quantity of finely divided carbon from whatever source invariably produces defective castings of the kind described if the carbon is long in contact with the metal in the furnace. It has also been learned that silicon carbide used as a constituent of the furnace lining, or for patching purposes, is capable of producing the same result. Crucibles containing silicon carbide and used in the normally oxidizing atmosphere of a fuel-fired furnace are occasionally responsible for defective castings of the same or a similar nature. Fortunately the silicon carbide itself is usually covered with a refractory glaze, so that there is seldom difficulty from this cause, but if an active flux, such as fluorspar or soda ash, is used with the metal, the glaze is destroyed and the characteristic worm-eaten,

coarsely crystalline castings result.   If the metal contains a large percentage of lead the effect is intensified by the fact that lead has a strong solvent action on silicon carbide.

As a result of these experiences and for a number of other reasons it was thought that the presence of metallic silicon in the brass might be responsible for the difficulty.   In the cases where carbon was apparently the source of trouble it was believed that the intimate mixture of carbon with siliceous material, such as molding sand from scrap metal or slag from the furnace lining, floating on the metal directly beneath the intense heat of the electric arc, might have resulted in the reduction of silicon and its subsequent solution in the brass.

A few years ago analytical methods for the determination of small quantities of silicon in brass were not so sensitive as they now are and no silicon was detected in any of this defective metal by the methods then in use.   However, in a sample of the metal sent to Professor Chamot of Cornell University for quantitative spectroscopic study as much as 1 per cent. of silicon was found in segregated portions of the casting.[2]   Of course the average silicon content of the metal as it would be sampled for chemical analysis was not anywhere near so high.   In fact it seemed probable that the silicon, if present at all, amounted to something less than 0.1 per cent. in the worst cases of contamination.

In the foundry with which the authors of this paper are associated, methods of metal control for several years past have been based on the assumption that metallic silicon dissolved in the brass is exclusively responsible for this particular defect in brass castings.   Working on this theory it has been found possible to keep out of trouble without in any way modifying the naturally reducing atmosphere of the electric furnace and consequently without sacrificing the advantages of such an atmosphere.   The metal produced in this way is in every respect of the highest quality obtainable from the alloys in use, judging from published data covering the properties and microstructure of such alloys.

SILICON IN COPPER AND COPPER ALLOYS

So far as the surface effect on the castings is concerned, the detrimental influence of silicon in a leaded brass or bronze is well known. According to Bamford[3] silicon is not a suitable deoxidizer for brass or bronze, or for any alloy containing lead, as it causes excessive drossing due to the formation of lead silicate.   Thews[4] says that, although silicon is a better deoxidizer than phosphorus, it cannot be used if lead

[2] J. Papish, private communication.

[3] T. G. Bamford: Indentify Impurities by Simple Tests.   *Foundry* (1928) **56**, 640.

[4] E. R. Thews: Alloys Affect Properties.   *Foundry* (1928) **56**, 534.

is present, because it forms compounds with the lead which cause excessive foaming of the alloy and the production of porous castings.   Vickers[5] says that as a trouble-maker silicon is worse than aluminum in the case of the ordinary red metals used in most brass foundries because a little silicon and a little lead together produce a large amount of dross, which is precipitated on the surface of the castings in the form of a grayish powder and produces pits too deep to be machined away.

Many other instances might be cited to show that progressive foundrymen realize the unwisdom of adding silicon to brass, regardless of melting conditions, but these are all concerned with the dross produced when silicon and lead come together and have no direct bearing on any effect silicon may have on the grain structure of the metal.   It has been the authors' experience that the imperfect crystalline structure is always to be found in cases where silicon is responsible for a drossy casting surface, but that, with decreasing percentages of silicon, the defective structure persists long after an apparently perfect surface is regained.   The literature seems to be void of useful information regarding the influence of silicon on the structure of brass, nor are there data as to the minimum percentages of silicon or of lead that will result in the surface imperfections described by the authors cited.

The influence of silicon in copper alone and in the so-called silicon bronzes is better understood.   According to Guillet and Portevin[6] silicon forms a solid solution with copper, with a maximum concentration of 4.5 per cent. silicon.   Bassett[7] says that silicon hardens and strengthens copper about two and one-half times as effectively as tin.   Vickers[8] recommends silicon as a deoxidizer for copper castings and mentions silicon bronze as having great strength and tenacity, specifying an analysis of approximately 97 per cent. copper, about 1 per cent. each of tin and zinc and 0.05 to 0.07 per cent. silicon.   Bolton and Weigand found that 0.03 per cent. of silicon in alloys low in lead seemed to have no appreciable influence on the properties of the metal.   In his discussion of their paper, L. W. Spring[9] described an experience in which small percentages of silicon caused leakers in castings containing 85 per cent. copper, 5 per cent. tin, 5 per cent. lead and 5 per cent. zinc.   By adding varying amounts of silicon to new metal of this same composition, Spring found that silicon in excess of 0.04 per cent. caused a noticeable increase in the proportion of leaky castings.

[5] C. Vickers: Metals and Their Alloys, 704.   New York, 1923.   H. C. Baird & Co., Inc.

[6] L. Guillet and A. Portevin: Introduction to the Study of Metallography and Macrography, 202.   London, Bell, 1922.

[7] W. H. Bassett: Copper and Copper Alloys.   *Min. & Met.* (1928) **9**, 171.

[8] C. Vickers: Op. cit., 347.

[9] L. W. Spring: *Trans.* A. I. M. E., Inst. Metals Div. (1929) 492.

Factors Influencing Grain Size

It is in these minute percentages of silicon and their possible effect on the structure of the alloy that we are particularly interested. In any study of alloy structure it is necessary to bear in mind that a number of factors have a substantial influence in determining the arrangement and shape of the crystal grains. Guillet and Portevin [10] make the statement that the number of grains in any given volume of an alloy depends upon:

1. The speed of spontaneous formation of centers of crystallization; viz., the increase in the number of centers of crystallization per unit of time per unit of mass.

2. The velocity of crystal growth from these centers.

3. The time available for crystal growth after the nuclei begin to form and before the metal is entirely solid.

When the nuclei begin to form the rate at which they form is very low while their velocity of growth is at a maximum. As the temperature falls the rate of formation increases while the velocity of growth decreases.

Guillet and Portevin further observe that, other conditions being constant, the number of grains in an alloy is also dependent on its chemical composition, small quantities of foreign substances being able to alter completely the number and, consequently, the size of the crystal grains of alloy. Usually several impurities are present and their combined effect may considerably modify the result that might be expected from the examination of the effects produced by the single impurities. It may happen that the addition of a substance to an alloy induces the solution of a third substance, or that two impurities separately soluble in the first metal in the solid state may form a definite compound when both are present. Very little reliable information has been obtained with regard to these effects.

It is evident that, in investigating the influence of a single impurity, it is of great importance to use an alloy of otherwise high purity and to carefully control the pouring temperature and the rate at which the metal cools in the mold.

Experimental Procedure

Most of the experimental work described in this paper was done with an alloy which normally contains 79 per cent. copper, 2.5 per cent. tin, 0.5 per cent. nickel, 10 per cent. lead, 8 per cent. zinc. Virgin metals were used; the silicon employed was approximately 99 per cent. pure.

In the first experiments the alloys were made and treated in a small gas furnace, using a No. 12 crucible. Regular crucible covers and various molten covers, such as borax, were tried but it was impossible to get

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[10] L. Guillet and A. Portevin: *Op. cit.*, 70.

consistent duplication of results.   Consecutive heats, melted apparently under identical conditions, resulted in metal that varied noticeably in structure and other properties.   Finally a laboratory arc furnace (Fig. 1) of the rocking type was constructed and used for all subsequent experiments. There was no further difficulty in duplicating results.   This furnace had a capacity of 500 g. of the alloy and was automatic in its operation except that it was rocked by hand.   During melting, the furnace was closed and, while no gas analyses were made, it seems fair to assume that its atmosphere was rich in carbon monoxide.   At any rate the furnace gases burned freely when allowed to escape into the air.

FIG. 1.—ROCKING ELECTRIC FURNACE, LABORATORY SIZE.

With the exception of a few chill castings, all specimens were cast in green sand, in the form of rectangular bars about 4 by $\frac{3}{4}$ by $\frac{1}{2}$ in. As a result of experiment, 2100° F. was chosen as a standard pouring temperature except in cases where the temperature was deliberately varied.   The effect of varying the pouring temperature is illustrated in Figs. 2 to 6, inclusive, in which the temperature was varied from 1800° to 2200° F. by 100° F. steps.   The etching reagent and the time of etching was the same in all cases.   The metal was virgin alloy containing 2.5 per cent. tin and 10 per cent. lead.   At the higher temperatures the lead distribution is poor and the metal deeply etched, while at the lower temperatures the lead is more evenly distributed and the metal much more resistant to the etching reagent.

In studying the effect of silicon, several series of alloys were made, beginning with pure copper and introducing the other constituents one at a time, adding each in such proportions that its ratio to each other constituent was the same as in the complex alloy analyzing: copper,
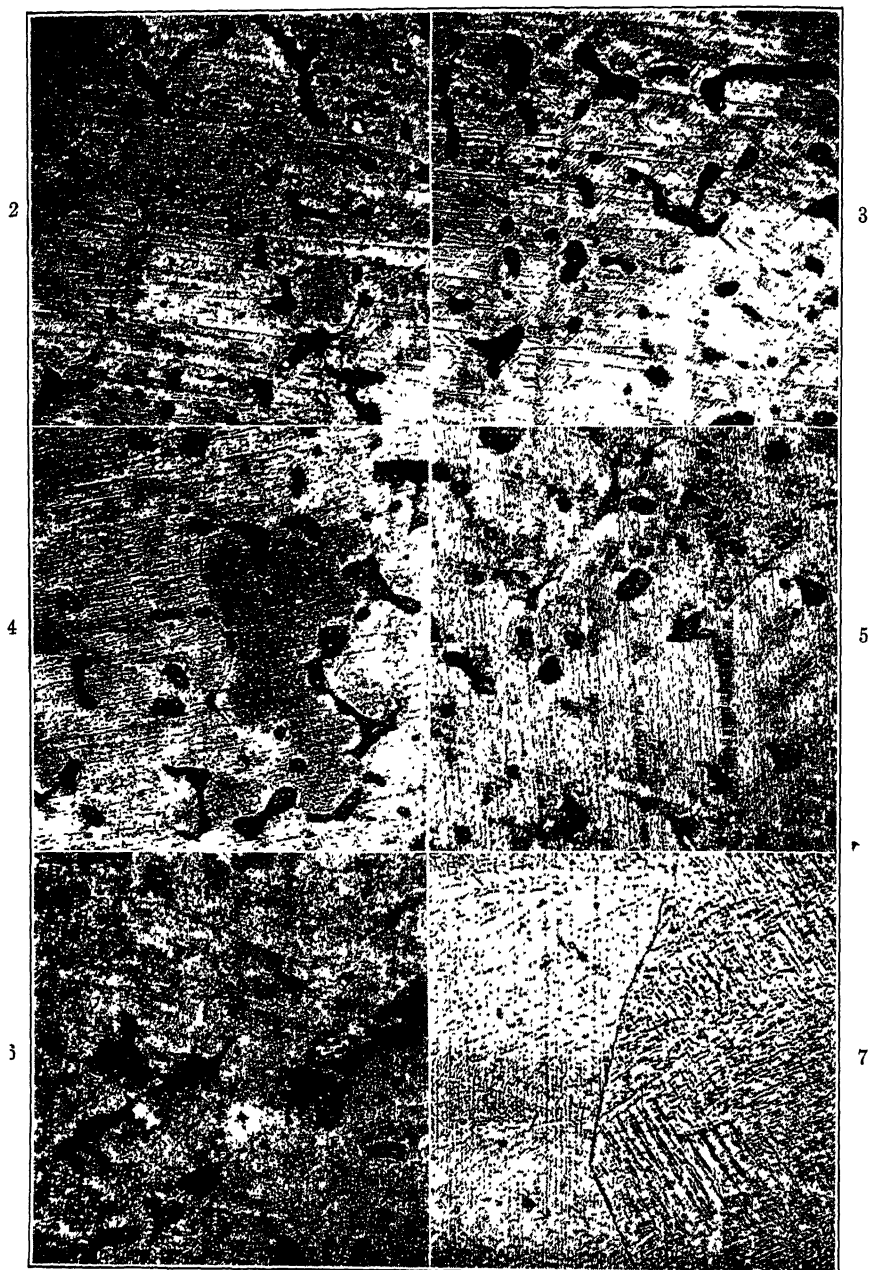
Fig. 2.—79 Cu, 2.5 Sn, 0.5 Ni, 10 Pb, 8 Zn, poured at 1800° F.   × 250.
Fig. 3.—Same as Fig. 2, poured at 1900° F.   × 250.
Fig. 4.—Same as Fig. 2, poured at 2000° F.   × 250.
Fig. 5.—Same as Fig. 2, poured at 2100° F.   × 250.
Fig. 6.—Same as Fig. 2, poured at 2200° F.   × 250.
Fig. 7.—90 Cu, 9 Zn, 1 Si.   × 500.

79.0 per cent.; tin, 2.5; lead, 10.0; zinc, 8.0; nickel, 0.5.   The base alloy of each series was thus as follows:

A. Pure copper
B. 90.8 per cent. Cu, 9.2 Zn
C. 96.9 per cent. Cu, 3.1 Sn
D. 88.3 per cent. Cu, 8.9 Zn, 2.8 Sn
E. 79.5 per cent. Cu, 2.5 Sn, 10 Pb, 8 Zn,
F. 79.0 per cent. Cu, 2.5 Sn, 10 Pb, 8 Zn, 0.5 Ni
G. 88.8 per cent. Cu, 11.2 Pb
H. 81.5 per cent. Cu, 10.3 Pb., 8.2 Zn
 I. 86.5 per cent. Cu, 10.9 Pb., 2.6 Sn

To each of these base alloys silicon was added in amounts varying from 0.05 to 1.00 per cent., although in most cases only the lower percentages were studied.   All alloys were carefully examined for the appearance of any constituent that might indicate the segregation of silicon. No such constituent was found in any case.

Metallographic samples were etched in ammonium persulfate of standard strength for a uniform time of four minutes each.

EXPERIMENTAL RESULTS

The addition of silicon to pure copper disclosed nothing not already described by previous investigators.   The addition of silicon to the alloy containing 90.8 per cent. copper and 9.2 per cent. zinc increased its Brinell hardness and apparently improved its structure.   There was no evidence of intercrystalline fissures.   Fig. 7 shows a crystal boundary in a sample containing 1.0 per cent. silicon.

With 96.9 per cent. copper, 3.1 per cent. tin, the addition of silicon decreased the Brinell hardness up to 0.25 per cent. silicon without noticeably impairing the structure.   Further additions up to 1.0 per cent. silicon increased the Brinell hardness to a point some 20 per cent. above the hardness of the original alloy and possibly resulted in a slight improvement in the structure.

When lead was added to the copper-zinc alloy, yielding 81.5 per cent. copper, 8.2 per cent. zinc, 10.3 per cent. lead, the addition of as little as 0.05 per cent silicon caused the formation, in the central protion of the casting, of a very closely knit dendritic structure of bright yellow crystals containing very little lead.   The outer skin of the casting, to a depth of ⅛ inch or more, contained most of the lead and was gray in color.   The segregation of the lead was very pronounced with a sharp line of demarcation between the gray and the yellow structures.   Figs. 8 and 9 show respectively the structure of the central portion of the casting without silicon and with silicon.

In the copper-tin alloy the effect was very different.   When 0.05 per cent. silicon was added to 86.5 per cent. copper, 2.6 per cent. tin, 10.9
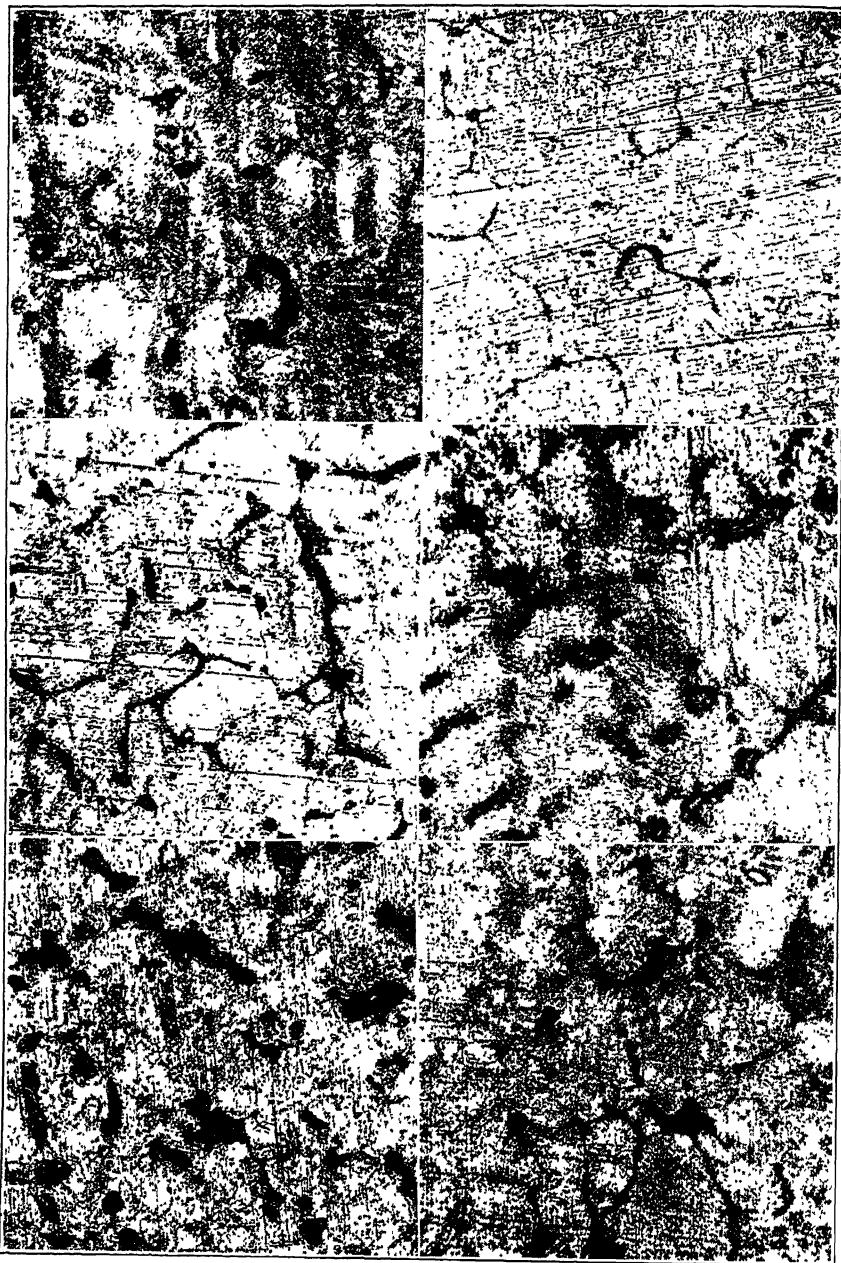
Fig. 8.—81.5 Cu, 10.3 Pb, 8.2 Zn.   × 250.
Fig. 9.—81.5 Cu, 10.3 Pb, 8.2 Zn, 0.05 Si.   × 250.
Fig. 10.—86.5 Cu, 10.9 Pb, 2.6 Sn.   × 250.
Fig. 11.—86.5 Cu, 10.9 Pb, 2.6 Sn, 0.05 Si.   × 250.
Fig. 12.—79 Cu, 2.5 Sn, 0.5 Ni, 10 Pb, 8 Zn, poured at 2070° F.   × 250.
Fig. 13.—79 Cu, 2.5 Sn, 0.5 Ni, 10 Pb, 8 Zn, 0.05 Si, poured at 2000° F.   × 250.

per cent. lead, the lead distribution became less regular, the metal more easily attacked by the etching agent and the casting unsound throughout (Figs. 9 and 10).

The addition of silicon to 88.3 per cent. copper, 2.8 tin, 8.9 zinc produced much the same result as when either zinc or tin was present alone. The alloy became harder and no detrimental effects were observed. When lead was added to this alloy the effect of 0.05 per cent. silicon was very pronounced (Figs. 12 and 13). Intercrystalline fissures developed to a marked degree and the lead distribution became irregular.

While the photomicrographs are interesting and quite necessary to an adequate understanding of the alloy structure, in most of the experiments performed the appearance of the fractured sample, as seen by the naked eye, is more enlightening and offers better evidence as to the effect of impurities on the soundness of the metal. Unfortunately, we did not have available the necessary equipment for taking macrographs, but even these would lose much of the desired effect because of the absence of color. An examination of the fractured samples shows that the normal base alloy, containing 10 per cent. lead, is fine grained throughout and a light gray in color. If poured at 2100° F. or above, the center portion contains large dendritic crystals of a yellow color set in a gray matrix. Metal containing silicon 0.05 per cent. or above shows a fracture of massive dendritic crystals with clearly visible intercrystalline fissures, the latter partly filled with fine-grained gray crystals. In this case the large crystals may have almost any color from a light yellow to a deep brown, presumably due to surface tarnishing by the infiltration of air through the fissures while the casting is still hot. If the metal is cast cold the dendritic crystals are much smaller and the fissures less evident. If the metal is chill-cast, the fracture appears entirely normal, although as much as 0.10 per cent. silicon may be present.

A series of alloys was run with varying percentages of lead and silicon to determine minimum percentages at which detrimental effects of the combination were apparent. The photomicrographs of these samples showed nothing of particular interest but visual examinations of the fractures indicated that at 2 per cent. lead, 0.05 per cent. silicon is sufficient to cause trouble, while at 1 per cent. lead, 0.05 per cent. silicon, the metal looks sound. At higher percentages of lead, up to 10 per cent., silicon varying down to a minimum of 0.03 per cent. produces the characteristic coarse, fissured structure. It is quite possible that, under favorable conditions, even smaller proportions of silicon may produce defective castings.

Another series of alloys was made to determine the influence of nickel in the presence of silicon. Samples were cast both with and without silicon, containing 0.5, 1.0, 3.0 and 5.0 per cent. nickel. The percentage of silicon used was 0.05. The photomicrographs were not
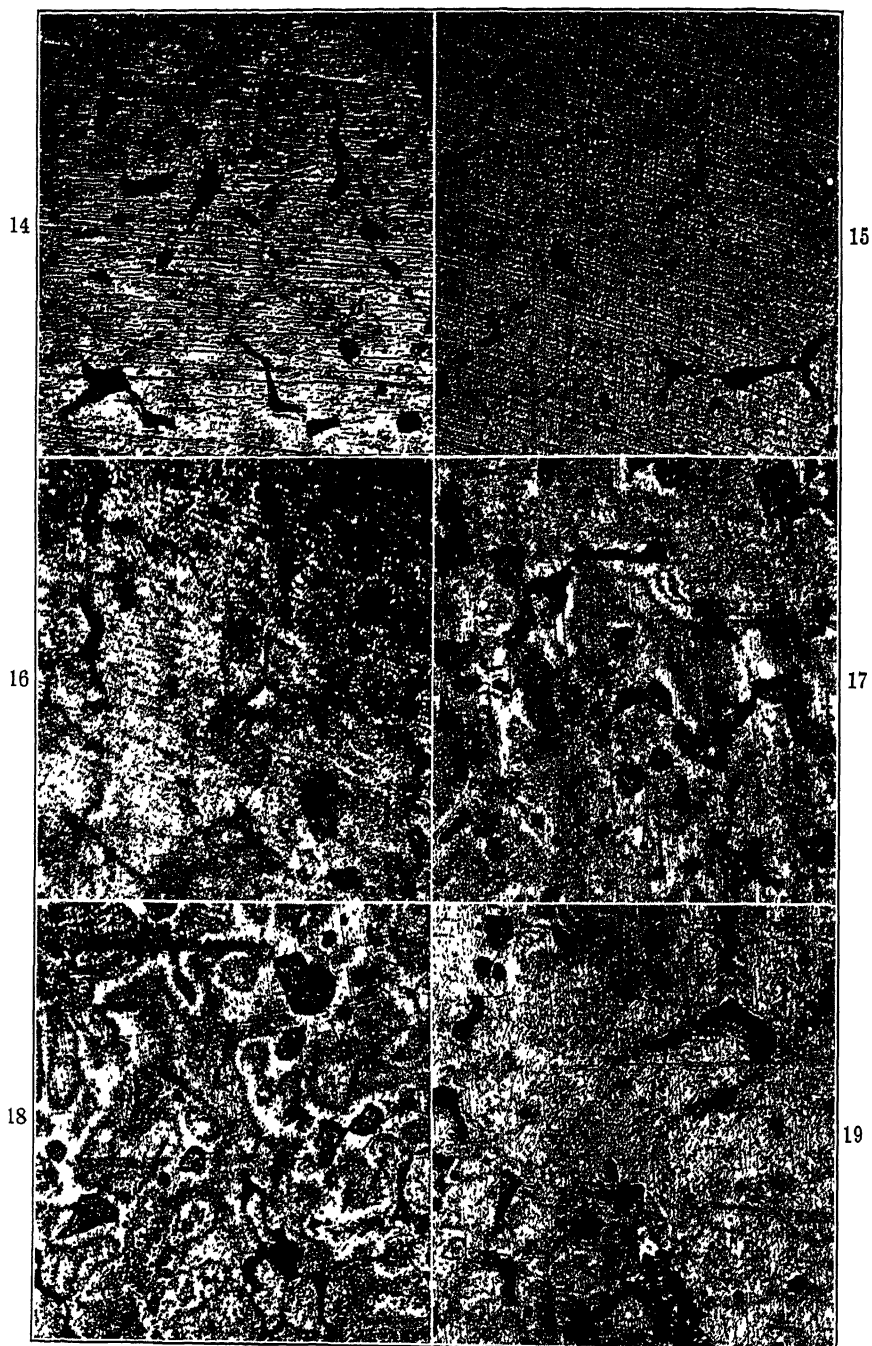
FIGS. 14–19.—CAPTIONS ON OPPOSITE PAGE.

particularly enlightening although the two extremes are given herewith as a matter of interest (Figs. 14 and 15). Samples containing silicon with 0.0, 0.5, and 1.0 nickel showed a very defective structure to the naked eye, although the last-named was a noticeable improvement over the first two. Samples containing 3.0 and 5.0 per cent. nickel apparently were perfectly sound and had the normal fine-grained gray fracture characteristic of the base alloy.

SOURCES OF SILICON AND ITS REMOVAL

Assuming that the detrimental effect of silicon in very small quantities when present in an alloy of the type here considered, is granted, the practical foundryman will have two important questions to ask: (1) Where does the silicon come from? (2) How can I get rid of it?

Silicon may enter the foundry melt from a variety of sources. Obviously silicon-copper should never be used as a deoxidizer with alloys containing as much as 2 per cent. of lead. The use of scrap copper which has been deoxidized with silicon or the use of miscellaneous scrap or turnings that contain silicon bronze may spoil the foundry castings directly or through the medium of composition ingot in which such scrap has been used without adequate refining. All of these things have happened. The most likely source of trouble with an electric furnace is in the furnace itself. Carbon or carbonaceous material, such as oil for example, should be carefully avoided in making up the foundry charge. Graphite electrodes used in the arc furnace will not be a source of trouble provided the furnace is operating with a free-burning arc, but will deposit carbon on the metal in cases where a low supply-voltage results in a hissing, smoky arc. Silicon-carbide refractories in contact with the metal are not necessarily injurious but, under the proper conditions, may be seriously so and should be used with much discretion.

To illustrate the fact that a mixture of carbon and siliceous material will spoil otherwise good metal melted in contact with such a mixture under a reducing atmosphere, a sample was made up, using virgin metal melted in the laboratory arc furnace. The metal was covered throughout the heat with a thin layer of silica sand mixed with finely divided graphite. The fracture of the resulting casting was very bad indeed and the photomicrograph shown in Fig. 16 exhibits the char-

FIG. 14.—79.5 Cu, 2.5 Sn, 10 Pb, 8 Zn, POURED AT 2100° F.   × 250.
FIG. 15.—77 Cu, 2.25 Sn, 5 Ni, 8.75 Pb, 7 Zn, 0.05 Si, POURED AT 2100° F.   × 250.
FIG. 16.—79 Cu, 2.5 Sn, 0.5 Ni, 10 Pb, 8 Zn, MELTED WITH CARBON AND SILICA SAND; POURED AT 2100° F.   × 250.
FIG. 17.—SAME METAL AS FIG. 16, AFTER REMELTING WITH BaSO₄ FLUX; POURED AT 2100° F.   × 250.
FIG. 18.—79 Cu, 2.5 Sn, 0.5 Ni, 10 Pb, 8 Zn, 0.1 Al, POURED AT 2100° F.   × 250.
FIG. 19.—SAME METAL AS FIG. 18, AFTER REMELTING WITH BaSO₄ FLUX; POURED AT 2100° F.   × 250.

acteristics peculiar to silicon contamination. Analysis showed silicon 0.055.

Obviously the best way to avoid trouble with silicon is to keep it out of the metal in the first place and this can ordinarily be done if the foundryman is familiar with the probable sources of contamination. Since silicon oxidizes readily it can be removed from contaminated metal by melting in a strongly oxidizing atmosphere. This is expensive because zinc and other desirable elements are oxidized at the same time. If the contamination is not too serious, enough of the silicon can be removed by melting in an electric furnace, the atmosphere of which has been rendered slightly oxidizing by admitting air. This is not quite so bad but does result in enough oxidation of zinc to partly offset the usual advantage of electric-furnace melting.

What is needed is a selective oxidizing agent, something that will oxidize silicon without affecting zinc. Such an agent is available in any of the alkali or alkali-earth sulfates, which, in the presence of silicon, aluminum, iron or other easily oxidized elements, give up their oxygen and are reduced to sulfides. The mechanism of this reaction and the technique of its use are matters which, for lack of space, will have to be discussed at another time. It has been used in a number of foundries for several years. Sodium sulfate is probably the most effective one of the group but has the disadvantage that it forms a liquid slag, difficult to skim from the molten metal. Barium sulfate, in the form of water-ground, water-floated barytes, is perhaps the most suitable for ordinary use.

Fig. 17 shows the microstructure of some of the contaminated metal illustrated in Fig. 16, after remelting in the same laboratory arc furnace (reducing atmosphere and all) with 1 per cent. of barium sulfate. The fracture of the metal after this treatment was excellent and the casting appeared to be entirely sound in every respect. The analysis of the metal before and after treatment follows:

	Before Treatment, Per Cent.	After Treatment, Per Cent.
Copper.	79 57	79.65
Tin...	2.67	2.60
Lead..	9 57	9 60
Zinc.. ..	8 01	7.90
Silicon.	0 05	0 018
Sulfur.	0.009	0 09
	99.88	99 86

Approximately 65 per cent. of the silicon present was removed by the treatment. The metal picked up a considerable amount of sulfur from the sulfate flux. While this is considered undesirable by some author-

ities, the authors believe that sulfur up to 0.10 or 0.12 per cent. does no harm in an alloy of this character. It certainly has some tendency to refine the grain of the metal and does not seem to possess any off-setting disadvantages. Most of the sulfur can be removed, if desired, by the subsequent use of soda ash.

As a further illustration of the effectiveness of a sulfate flux, Fig. 18 shows a sample of the base alloy, made up from virgin metal to which 0.10 per cent. of aluminum had been added. Intercrystalline fissures are plainly visible and the fracture very bad. Fig. 19 shows the same metal after remelting with barium sulfate. The metal appeared to be sound in every respect.
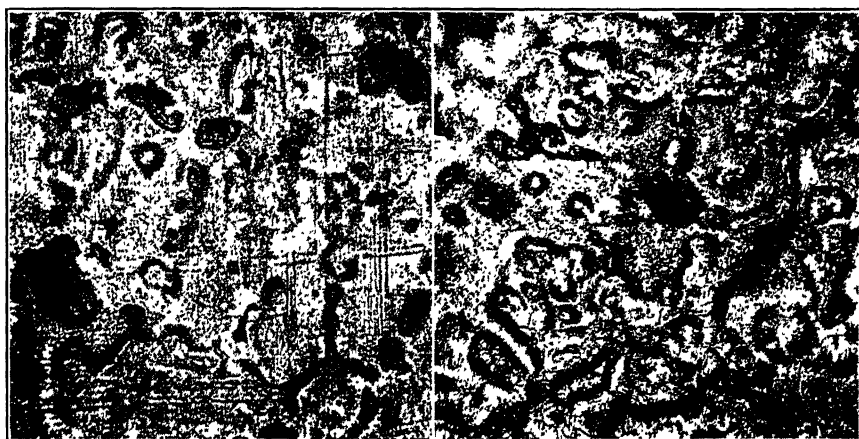
FIG. 20.—79 Cu, 2.5 Sn, 0.5 Ni, 10 Pb, 8 Zn, WITH 0.2 Sb ADDED, POURED AT 2050° F.   × 250.

FIG. 21.—79 Cu, 2.5 Sn, 0.5 Ni, 10 Pb, 8 Zn, WITH 0.6 Sb ADDED, POURED AT 2050° F.   × 250.

Figs. 20 and 21 are given as a matter of interest, to show the peculiar effect of antimony on the microstructure of the base alloy. In each case the macrostructure was normal. No further study of antimony was made.

DISCUSSION OF RESULTS

The authors recognize that much of the work described in this paper is qualitative rather than quantitative. Neither the time available nor the facilities permitted a close determination of all of the factors involved. An actual test of the effect of different furnace atmospheres, accompanied by gas analyses, would have been desirable. A thermal study of the solidification process in alloys containing varying percentages of silicon and of nickel would add appreciably to the value of the data. The furnace used was too small for casting reliable tensile-test bars, the results from which might perhaps be more convincing to those who are in the habit of depending largely on such tests. A variety of other

tests and determinations could have been made to advantage. It is hoped that others will add to this information from time to time so that it will ultimately be possible to confirm or modify our present conclusions as this additional information may indicate.

The conclusions drawn at this time are undoubtedly influenced somewhat by our years of experience with the problem as well as by the results of our experimental work. It is felt, however, that there is ample evidence to support their validity and that any modifications which may later be made in them will be changes in degree rather than kind.

SUMMARY

1. Very small percentages of silicon in foundry brasses and bronzes containing copper, tin, lead, and zinc have a tendency to produce a coarse dendritic structure, with intercrystalline fissures, which causes castings made from such metal to be weak and porous.

2. Alloys of copper with zinc or tin, or zinc and tin, in the proportions described in this paper, but containing no lead, are hardened and strengthened by the addition of small percentages of silicon. There is no apparent detrimental effect on the structure of the metal.

3. In an alloy containing approximately 82 per cent. copper, 8 per cent. zinc, 10 per cent. lead, without tin, the addition of 0.05 per cent. silicon results in a pronounced segregation of the lead in the outer skin of the casting while the central portion, although dendritic, is closely knit and tough. There is no appearance of intercrystalline fissures but the outside surface of the metal is pitted and has the characteristic discoloration produced by the interaction between lead and silicon.

4. An alloy containing approximately 86.5 per cent. copper, 2.5 per cent. tin, 11 per cent. lead, without zinc, becomes coarsely dendritic, with intercrystalline fissures and segregation of lead, when small percentages of silicon are added to it.

5. An alloy containing approximately 79.5 per cent. copper, 2.5 per cent. tin, 8 per cent. zinc, 10 per cent. lead, to which 0.05 per cent. silicon has been added, becomes very coarsely crystalline and develops large fissures between the crystals. The metal is so bad as to be quite unfit for ordinary casting purposes.

6. An alloy containing as little as 2 per cent. lead with 0.05 per cent. silicon shows the defective structure characteristic of silicon contamination. At 10 per cent. lead, 0.03 per cent. silicon is sufficient to show a detrimental effect.

7. Chill-casting an alloy containing silicon results in a fine-grained structure that is apparently normal. If the metal is cast in green sand at varying temperatures the effect of silicon on the structure becomes progressively less marked as the casting temperature is lowered.

8. The addition of nickel to an alloy containing silicon progressively reduces the effect of the silicon on the structure, although, with a silicon content of 0.05 per cent., the effect of the nickel is not pronounced until 1 per cent. of nickel has been added. At 3 per cent. nickel the influence of the silicon is apparently entirely obscured and a very fine-grained structure results.

9. The use of an alkali sulfate, such as anhydrous sodium sulfate, or an alkali-earth sulfate, such as barium sulfate, as a flux in an electric furnace, tends to eliminate the silicon by selective oxidation without appreciably affecting the normal constituents of the alloy.

10. The defective structure described, which the authors believe to be the same as that previously described by Bolton and Weigand and termed by them "incipient shrinkage," is not due, in any direct way, to the presence of carbon monoxide in the furnace atmosphere. It can, however, be rectified or prevented by melting the metal under an oxidizing atmosphere, which prevents the reduction of silicon or oxidizes it if already present.

11. The most common source of silicon contamination in foundry brass is by reduction of silicon in the melting furnace. A furnace atmosphere rich in carbon monoxide permits such a reduction to take place if an intimate mixture of finely divided carbon with a siliceous material is present. In the absence of solid carbon there is no evidence of silicon reduction by the carbon monoxide atmosphere.

12. Other occasional sources of contamination are silicon copper or silicon bronze entering into the furnace charge, or silicon carbide used as a refractory in the furnace lining. Trouble from silicon carbide is aggravated by the use of fluxes in the furnace, since these tend to destroy the protective glaze. It also appears that lead has a solvent action on silicon carbide.

13. The authors believe that silicon tends either to obstruct the formation of crystal nuclei in the molten metal or to prolong the period during which part of the metal is molten after it enters the mold. In this way a few crystals grow to large size and the shrinkage of these crystals results in openings or intercrystalline fissures. Incipient shrinkage is probably as good a term as any for this phenomenon. Anything that tends to shorten the freezing time, such as chill-casting, tends to offset the influence of the silicon. The addition of another constituent, such as nickel, which tends to form more nuclei, also tends to prevent the detrimental effect of the silicon.

DISCUSSION

J. W. BOLTON, Cincinnati, Ohio (written discussion).—In this paper the deleterious effects of silicon contamination as obtained in furnaces operating under reducing atmosphere seem more serious than the effects noted by the speaker and coworker, who used

a carefully controlled neutral (maximum CO_2) atmosphere in their experiments on the action of silicon. Further, the paper indicates the ease with which inadvertent silicon contamination can be obtained in the indirect-arc types of furnace, and offers a type of cure for the trouble that may not be altogether satisfactory.

In general we agree with most of Mr. St. John's conclusions, although we would prefer the opportunity of examining test data on changes in porosity in commercial castings, tensile strength (which, incidentally, often is an excellent index of porosity) the actual furnace atmosphere, specific gravity and the like.

There is one thing, we believe, that Mr. St. John's paper neither proves nor disproves—and remember that most of these are single experiments, lacking the cumulative action of repeated remelts, which emphasize effects of reducing atmospheres.

That thing is, that (as the speaker, in common with a number of others, has shown) the effects of continued exposure to atmospheres rich in carbon monoxide in itself often causes incipient shrinkage and lowered strength, and when the condition is at all aggravated, porosity—and this in certain alloys that are practically free of silicon. This was indicated in a paper presented last year.[11] The analytical methods used were very carefully checked as follows:

1. Blanks were run including all the reagents, etc., involved. A low and constant blank was obtained.

2. Porous metal melted under atmospheres rich in CO was analyzed for silicon, and well under 0.01 per cent. silicon (0.003 per cent., I believe) was found.

3. Sound metal was analyzed and only traces were found, just as in the unsound metal.

4. Only one loophole remained—did we get all silicon present properly oxidized to silica by the reagents? We added a small weighed amount of silicon-bronze drillings of known analysis to a weighed bronze sample in a beaker and analyzed the mixed drillings. We got all the silicon we added—proving the analysis and methods correct.

I would like to ask Mr. St. John two questions: When adding silicon to metal melted under neutral atmospheres we got quiet metal in the pot. Melting under reducing atmospheres, and no silicon in the final alloy, we got wild, gassy, rolling metal. What stirred the metal up this way? If not reducing gases of some sort, what came out of metal melted under reducing conditions that burned, as described by Boeck last year?

The following is quoted from a letter from the eminent British metallurgist, H. C. Dews: "There are still many questions requiring solution; for example, what is the brown coloration one finds on breaking open bad bronze? If it is oxide, why is it most prevalent when the bronze is melted under a reducing atmosphere? If it is not an oxide, what is it? Even in an oxidizing atmosphere, if the casting temperature is not correct one still finds the same coloration."

W. F. GRAHAM, Mansfield, Ohio.—The subject of the paper by Messrs. Bolton and Weigand (p. 368) and that by Messrs. St. John, Eggleston and Rynalski is opening up a definite metallurgical appreciation of what happens in melting red brass. I shall start with Mr. St. John's paper.

I agree with the first and second items of the summary in his paper. On the third item we do not have any particular information on the first sentence as given by Mr. St. John, but on the second sentence our experience is that silicon is likely to be more deleterious as a surface destroyer than as a structural destroyer, which is somewhat contrary to Mr. St. John's exposition, I believe.

On the fourth item we have no data. We are agreed on the fifth item. We have no data on the sixth. On the seventh we are agreed and we also would like to make the

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[11] J. W. Bolton and S. A. Weigand: *Op cit.*

comment that considerable relief can be obtained by lowering the pouring temperature of contaminated metals. The same thing applies to a large contamination of phosphorus.

On the eighth, we believe it is reasonably due to the formation of the soluble nickel silicide, as in the Corson type of alloy.

On the ninth, we are more or less in disagreement on the more practical aspects of handling the barium sulfate in the indirect-arc type of furnace as regards its total action as compared, however, with the action in a crucible, which we find takes place very rapidly.

From ten to thirteen, we believe that there is considerable room for argument. While the theory of the formation of the intercrystalline fissure is a very nice one and a logical one, we are not so sure as to the effect of silicon *per se*. If there is any difference in opinion between Mr. St. John and Mr. Bolton, possibly the truth lies in the middle ground or in a definite combination of their two interpretations; for example, whether silicon makes bad brass or something producing silicon to make bad brass.

While we have had no analysis made of the kind that Mr. St. John has had made, we have not been able to find silicon in a considerable amount of a coarse structural metal, both deductively and inductively attacked. We have found a modification of this structure in other bad metal from the reducing type of melting operation. The metal is plainly gassed and exhibits a fracture characterized by countless spheroidal voids. The color is a golden one. This characteristic is eliminated by remelting in an oxidizing atmosphere. It would appear that in some cases, at least, some other theory than the silicon theory must apply. It appears that the occurrence of some furnace reaction or the liberation of some metallic contamination influence is the cause of the amount of gas dissolved in the metal. We have, in fact, always found so-called siliconized leaded red brasses extremely gaseous in both the ladle and the molten. That is more or less, as I understand it, in opposition to what Mr. Bolton said.

This gas may be CO. In freezing or passing through the freezing range some of the gas is forced out of the solution, leaving the metal porous. Possibly carbon or minute traces of aluminum silicate would create this effect. All of them, as well as the CO dissolved, are oxidizable.

If I may be able to express it, and I do not know whether I am able to convey the idea I have in mind, I do not think that CO *per se* is responsible for the condition that exists in the brass, but possibly CO under certain melting conditions, oily borings, granulated carbon of one kind or another included in the charge, something on that order, produces a secondary effect, or minute traces possibly of some other metallic reduced impurity, which then changes the crystal habit of the metal in the casting.

One thing more in relation to Mr. St. John's paper. We have found in both inductive and deductive work that silicon affects the surface more strongly and aluminum the structure. As little as 0.05 per cent. of aluminum if added to copper 81.5, tin 3, lead 7, zinc 8.5, a typical red brass, has caused 100 per cent. leak loss on the test bench. That was where we made the addition intentionally. The same amount of silicon, 0.05 per cent., caused only 16 per cent. leak loss, but 71 per cent. was rejected for surface conditions by the brass foundry inspection before entering into the machine shop.

Aluminum, on the other hand, caused only 14 per cent. rejection by the regular inspectors for bad surface conditions. That is a definite experiment which we believe can be verified easily in foundry operation.

There are two points in relation to Mr. Bolton's paper that I would like to comment on. The value or the proper use of his term "incipient shrinkage" is not clear in my mind. I may be splitting hairs. Possibly it conveys more to others than it does to me, but I do not like the term. I think that possibly it conveys only part of the story as regards the structure. I hope Mr. Bolton will be able to amplify that term or find

another one in the future that will be more conclusive to cover the condition that he speaks of, which does exist; there is no question about its existence.

It seems to me that he introduces an element of confusion between the incipient shrinkage idea and the oxidized idea, that is, conveys the idea that it is not possible to distinguish between the two. I believe they are very easily distinguishable by simple means, possibly by only fracturing the specimens. (See Fig. 22.)

I understood Mr. Bolton to say that the drop in zinc was a proof of oxidization. I do not believe that is any great proof of oxidization, because the zinc certainly can be boiled out, that is, volatilized out of the metal.

Fig. 22 shows sections of three little slabs of metal cast vertically as shown. The original magnification is about one diameter. First they were all sawed and fairly finely polished, and then deeply etched. They are of a red brass composition. I have not the exact figures, but it is a variation of 85-5-5-5. This is melted under reducing conditions (A). The swelling at the top is typical of gassed metal, or it might be called overpoled metal. We obtained it by use of a great deal of charcoal. It was melted in a laboratory furnace, gas-fired. Here are some of the fissures which Mr. Bolton calls incipient shrinkage. B shows the same metal melted under oxidizing
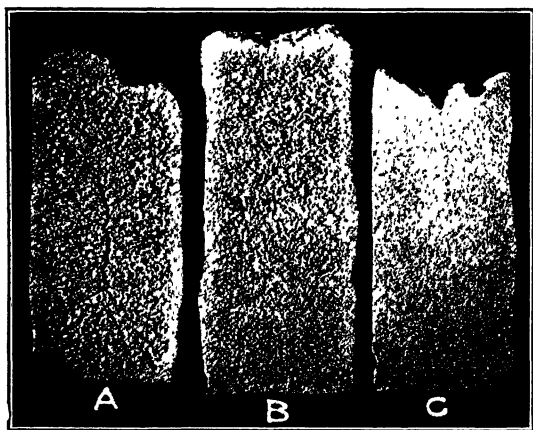
Fig. 22.—Sections of metal slabs cast vertically.

conditions. While it may not show particularly on the reproduction, the fracture can be distinguished very easily. This is oxidized metal and the reason we believe it to be oxidized metal is that we blew air into it and immediately poured it out into the sand mold.

C shows the same metal melted under what might be called normal or neutral conditions. There is an etching that is relatively uniform. The photographs give the distinction clearly.

Member.—How did you determine the neutral atmosphere for specimen C?

W. F. Graham.—That is simply a normal melting condition that was probably slightly on the oxidizing side. In other words, it is just about the same as you would melt brass in a crucible.

Member.—In Mr. Bolton's determinations, did he notice any difference in his ability to machine these specimens containing silicon as against those free from silicon?

J. W. BOLTON.—In Mr. Graham's discussion it is brought out that siliconized metal may be gassy. I do not think I made clear in my own discussion the various conditions that may prevail. In melting under a neutral atmosphere (by gas analysis), if the metal contains silicon it is not gassy—it does not kick around—whereas similar metal with silicon contamination melted under a highly reducing atmosphere will kick and boil in the ladle.

Regarding the term "incipient shrinkage," I might say a rose of any other name would smell as sweet, but I believe Mr. Graham has not clearly understood or interpreted my intent to characterize the effect rather than the causes by the term "incipient shrinkage." We are not trying to describe the causes by the term. We say the net effect is incipient shrinkage. By shrinkage hole or drawhole, the foundryman understands a jagged cavity, possibly with some dendritic formation projected into it. That is known as a shrink hole.

In cases where there is general porosity in the metal we usually have a condition much less aggravated than that noted in a shrinkage drawhole, but we have been able to prove that is the same phenomenon except that it is incipient.[12] I believe the dictionary says that "incipient" means just about to be, or just beginning to be, the condition to be described. Its application in the term "incipient shrinkage" therefore is obvious.

While the effect has been described as incipient shrinkage, the three causes that may be pointed out here are oxidizing atmospheres, or reducing atmospheres, or the presence of impurities, or a combination of these.

Regarding the questions about the loss of zinc not being a positive proof of oxidization, I will agree that that as stated is correct, and that it is my error in not making clearer why we said that was oxidizing. The metal in this state actually had air passed over it in the molten condition, and there was a slag formed, which makes it quite sure that it was exposed to oxidation, and it was partly oxidized.

H. E. WHITE, Zelienople, Pa. (written discussion).—In view of older practice it seems a paradox that silicon should be absorbed from linings, or reduced from silica and carbon under normal conditions in non-ferrous melting. Going back to the old type graphite-sand-clay crucible, the metal certainly was in contact with the same ingredients in neutral and reducing atmospheres. Silicon carbide is frequently found in old used crucibles which were originally free from it, the silicon carbide having been formed from the silicon and graphite under temperature. Other factors should then be considered for this particular case, such as the temperature of the electric arc and its effect on linings and metals, as the contamination is certainly present.

In the metallurgical manufacture of metallic silicon from silica and carbon the electric arc is necessary, and actual contact of silica with carbon is also necessary. Practically no reduction is done by carbon monoxide.

Referring to difficulty originating with oily borings and foundry sand on gates forming the typical silicon coating, is it not possible that some carbon monoxide may be broken down to carbon by the action of the arc, and used as a reducing medium?

A good many of our commercial fluxes bring about the same combination of materials mentioned; that is, silica and carbon. When used as a seal on crucibles, which in themselves sometimes contain silicon carbide, excellent metal is produced, while the same metal used in an electric-arc furnace lined with silicon carbide, or using silicon carbide as a patching cement, is frequently of questionable quality.

One of our largest foundries operated the two types of equipment on high-lead mixtures, extending over a period of six months, and finally found, after exhaustive tests, that the crucible melting gave the most uniform metal. This was somewhat similar to the U. S. Navy Yard experience with G metal.

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[12] J. W. Bolton and S. A. Weigand: *Op. cit.*

Some other factors, such as temperatures, might have been responsible for the lack of consistent results in the experimental procedure described using crucible melting.

There is only question regarding the work with barium sulfate: Is there any contamination by sulfur under the arc temperatures of the electric furnace?

One possibility of contamination by silicon from silicon carbide materials may be due to improper preparation of cheap cements formed of silicon carbide firesand Silicon carbide, and especially firesand as produced, usually has a surface coating of 0.2 per cent. to 0.6 per cent. silicon, and this has been known to run as high as 1 per cent. In the proper preparation of cements and refractory shapes from silicon carbide, this coating should be removed.

Furnace atmospheres and the zonal temperatures are probably more responsible for some of the conditions mentioned than any other factor. From a chemical standpoint this also seems most logical. Silicon carbide is broken down much more easily by lead peroxide than by lead oxide, according to the equation

$$SiC + 2PbO_2 = SiO_2 + PbO + CO$$
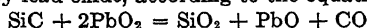
Similarly it seems improbable to expect

$$SiC + Pb = PbSi + C$$

as one would think considering reducing conditions. Free carbon has seldom if ever been observed under these conditions, although it has sometimes been found as a metal carbide.

It is more probable that

$$SiC + PbO = PbSi + CO$$
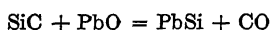
takes place, indicating that oxidizing conditions do have some effect on metal contamination.

To speak of oxidizing and reducing atmospheric conditions is rather vague and uncertain. Both conditions may occur during the same heat and frequently in different parts of the same furnace at the same time. Undoubtedly the sequence of their occurrence has a decided effect on contamination of the metal.

There is little question that lead and nickel in their pure state, under the proper conditions, will readily absorb metallic silicon. When we consider the absorption of silicon from silicon carbide by non-ferrous alloys containing lead and nickel we are pitting against each other on the one hand alloys which in themselves for the most part are chemical combinations and on the other hand a strong chemical combination of silicon and carbon. In this state of combination the absorption or combination power is much lower than that of the pure metals or elements.

It seems therefore that while the conditions causing silicon contamination have been somewhat defined, we are as yet rather uncertain as to the exact reason for this phenomenon, especially in so far as silicon carbide is concerned.

Mechanical inclusions of refractory particles such as silicon carbide have been observed in non-ferrous alloys, particularly in aluminum. In the latter metal these have appeared as minute particles showing hard spots when the casting is machined.

H. W. Maack, Chicago, Ill. (written discussion).—The authors' finding that the structure of copper-tin-zinc alloy without lead is benefited rather than harmed by small percentages of silicon but that with both tin and lead present, silicon is harmful, as several have stated, is interesting; also their finding that with 3 to 5 per cent. of nickel present the alloy was not affected by small amounts of silicon, though with smaller amounts of nickel, the structure was defective. It would appear that the effect of some of these metals on one another is complementary, and probably the effect of impurities such as silicon and aluminum is cumulative. That sodium sulfate and barium sulfate are effective in removing silicon from brass is worth knowing. We have tried calcium sulfate without much effect on the silicon content, but found considerable contamination of the brass with sulfur. The authors' conclusion that 0.10 or 0.12 per cent. sulfur is not harmful confirms our own experience.

The effect of furnace lining on contamination of the melt is a subject which deserves much study.

H. M. St. John.—Mr. Bolton has raised a point with regard to the tensile strength and porosity data on the samples described in our paper. It was mentioned in the paper that many additional data might have been taken to good advantage. I am sorry that we did not have time to do it. These additional data I hope to see supplied by someone else. They should be enlightening.

I am not prepared to discuss the question of accuracy in analysis for silicon. It is a long time since I did any analytical work of this kind and I am not particularlp expert on this subject. The analytical work mentioned in the paper was done by the Detroit Testing Laboratory. We checked their work carefully by sending them a variety of samples, some of which we knew contained silicon while others did not. We were unable to find the laboratory at fault in any case. The exact amount of silicon present is, of course, another matter, but whenever we knew there was silicon present the laboratory found it and when we had reason to believe there was no silicon the laboratory found none. This point we confirmed several times.

Several of the points mentioned by Mr. Bolton and Mr. Graham can be discussed under one head. It was brought out in our paper that the pouring temperature is very important. A coarse and discolored structure can be obtained with pure metal by pouring it too hot. This fact might answer a number of questions which have been asked where no information was given as to the temperature used. I shall make no attempt to answer either of Mr. Bolton's questions about wild metal. I would consider it presumptuous to attempt a solution for a described condition that one has not seen, and concerning which one has incomplete data. It is questionable whether the correct pouring temperature for any casting is the same when metal is melted under a reducing atmosphere as it is when melted under an oxidizing or a neutral atmosphere. In other words, if the atmosphere is varied and the pouring temperature held constant, would the result be a true comparison between the different atmospheres so far as their effect on a sound casting is concerned?

I have a distinct impression that in general an alloy melted under a reducing atmosphere should be poured at a lower temperature than the same metal melted under oxidizing or neutral atmospheres in order to produce sound castings. I am referring now to what foundrymen call spongy metal. To avoid such a condition, a lower pouring temperature should be used with reducing atmospheres. I have heard it said more than once by users of electric furnaces that the use of such furnaces has lowered their average pouring temperatures. If the pouring temperature is not lowered it is possible to produce defective metal, due to improper pouring temperature alone. Of course, this may not be a complete explanation of the points which have been raised, but it seems to be at least an important factor.

Mr. Graham mentioned that aluminum seemed to have the greater effect on the structure of the metal, while silicon had more effect on the surface. I cannot say that we noticed such a difference. Two samples, one containing silicon and the other an equal amount of aluminum—0.05 per cent. approximately in each case— do not show any great difference.

W. F. Graham.—That was judged by the pressure test, not by appearance.

H. M. St. John.—We should also bear in mind that we are not talking about exactly the same alloy, and while there does not appear to be such a difference between the alloys as would explain any considerable difference in results, still we are not entirely sure of this. Difference in behavior of the alloys used by Mr. Bolton and those used by ourselves might explain part of our difference in opinion.

With respect to the question regarding machinability, I can say that brass contaminated with silicon is more brittle, harder, probably has a higher tensile strength, less elongation and machines with more difficulty.

J. W. BOLTON.—Through investigation we found that when melting under a neutral atmospheric condition the pouring temperature range was very much wider than it was when we used reducing atmosphere. Sometimes, to get any good results at all under reducing atmosphere, we had to regulate pouring temperature very closely. The reasons are obvious—a critical cooling rate must be held to get anything like sound castings from gassed metal. The effects of pouring temperature had been considered all the way through in both the investigations and held nearly constant.

H. M. ST. JOHN (written discussion).—It should be borne in mind that there are several varieties of porosity commonly found in foundry brass and that these are due to diverse conditions. The type of porosity discussed in this paper is characterized by fissures, angular in shape and occupying the space between large dendritic crystals. The sort of porosity commonly attributed to gas escaping from the metal during solidification, where the voids are discontinuous and roughly spherical in shape, is an entirely different phenomenon. The latter type of porosity is frequently encountered in all sorts of alloys, melted in any kind of furnace. Its causes are not particularly obscure and its control in the foundry is a relatively simple matter.

Mr. Bolton states that our paper neither proves nor disproves that a furnace atmosphere rich in carbon monoxide may be responsible for incipient shrinkage, which we assume refers to porosity characterized by intercrystalline fissures. He is correct in this statement. The paper proves only that this type of porosity can be caused by the presence of small quantities of silicon in metal melted under an atmosphere rich in carbon monoxide, while precisely similar metal, melted under the same kind of atmosphere but containing no silicon, shows no evidence of porosity.

We have offered an explanation as to the manner in which silicon produces this effect and have endeavored to make this explanation inclusive enough to fit all of the facts which we have observed. It seems to us that we have succeeded in this effort. On the other hand, we have not yet heard or seen a plausible explanation of the manner in which carbon monoxide or any other gas could produce an effect so different from that which common experience has taught all foundrymen to expect when their metal is "gassed." If we are to believe that intercrystalline fissures are in some way due to the chemical action of carbon monoxide on constituents of the alloy, or on impurities present in it, we should be offered some experimental evidence that such action really takes place. The mere presence of carbon monoxide at the scene of the crime is not sufficient evidence of its guilt. It may be an accomplice but probably not a principal. In the absence of the principal the crime does not take place.

Melting Bearing Bronze in Open-flame Furnaces

By Ernest R. Darby,* Detroit, Mich.

IF the correct balance between fuel and air is maintained in an open-flame furnace,[1] little chemical action may be expected between the products of combustion and the metal being melted. Physical changes in the metal are the object of the melting operation, and indirectly, under certain conditions, may be the cause of subsequent chemical actions. If sufficient heat has been introduced into the metal to bring about the change from the solid phase to the liquid phase, and still further from the liquid to the vapor phase, the metal vapor in all probability will be carried from the furnace by the exhaust and rapidly combined with the oxygen of the outside air. The charge being melted in the furnace may contain elements which are chemically inactive at normal temperatures but which will form compounds at the elevated temperatures of the metal bath, or even at a lower degree. Such indirect chemical actions are very confusing and often lead to incorrect conclusions regarding furnace atmospheres.

In the open-flame furnaces used in the melting of bronze, the furnace atmosphere is spoken of as being either neutral, oxidizing or reducing in its effect upon the metal. A neutral atmosphere, as mentioned, is generally considered as the atmosphere of the furnace that will produce melted bronze, neither oxidized nor gassed. It is in effect an atmosphere which is not directly the cause of any chemical action. In such an atmosphere absolutely pure metals may be melted and poured without the absorption of gases or the formation of metallic oxide. The metal has undergone a simple, physical change.

An oxidizing atmosphere is one in which the air introduced to the furnace is in excess of that required to complete combustion of the fuel used. The oxygen of the excess air may combine with the metal being melted to form metallic oxide, which may or may not be dissolved by the metal. If an absolutely pure metal is melted in a furnace operating with such an atmosphere, a portion of the metal charged may be converted into metallic oxide, the amount depending upon the duration of the

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[1] The term "open-flame furnace" is meant to apply to furnaces using oil and gas as fuel, with the flame in direct contact with the metal. Crucible furnaces are not included in this article.

melting operation and the temperature to which the metal bath may be raised.   The metal has undergone a chemical as well as a physical change.

The atmosphere spoken of as being "reducing" is the direct opposite of the oxidizing one.   The reducing atmosphere is produced by an excess of fuel over that required to completely combine with the air of the furnace.   The resulting incomplete combustion gives rise to gases that are reducing in their action upon metallic oxides.   In an atmosphere of this kind metal containing quantities of oxide may be melted and the oxide reduced to metal by giving up its oxygen to the unburned fuel gases to assist in complete combustion.

SELECTING A FURNACE ATMOSPHERE

Of the three conditions of atmosphere mentioned, the most difficult to obtain in practice is the neutral one.   Since it represents an absolute balance between fuel and air, it is by nature very narrow between its marginal limits, so narrow, in fact, that one may consider it as but a line separating the broader fields of oxidation and reduction.   It is almost an impossibility in actual practice to operate an open-flame furnace on a theoretically neutral atmosphere, and even if such a condition could be effected, the task of determining it would be extremely difficult.   For this reason, the selection of a furnace atmosphere is reduced to the problem of determining whether an oxidizing or a reducing condition is the better for the purpose in mind.

Most bronzes, particularly those used for bearing purposes, readily absorb gas formed by incomplete combustion, the rate or amount of solution increasing rapidly with the increase in metal temperature, the duration of overheating, and the increase in explosion pressure of the incoming fuel.   Considering the melting operation as being divided into two periods, (1) that in which the metal is raised from normal temperature to the temperature of liquefaction and (2) that in which the excess heat necessary for handling and pouring is introduced, then the second period is the one in which a reducing atmosphere gives the greatest possibility of gas absorption.

Since the most harmful effect of gas is due to its precipitation at or near the temperature of solidification, with a reducing atmosphere there is little danger of gas absorption during the first period.   There is, however, in this period a possibility of the formation of sulfides, which subsequently may be absorbed by the melt.   This possibility is not serious if the fuel is the only source of sulfur, for few fuels used for melting purposes contain as much as 1 per cent. of this element.   Assuming 130 lb. of oil as the amount required to melt 1000 lb. of bronze, then with a 1 per cent. sulfur content, 1.3 lb. of sulfur must pass through the furnace. Not over one-tenth of this amount could possibly be absorbed by the

metal, which would represent but 0.013 per cent. of the 1000 lb. of metal melted. Such an amount in itself cannot be serious, but by accumulation through frequent remelting or by additions in some form with the metal charged the first period may be accompanied by considerable sulfur absorption.

Though the absorption of gas and the absorption of sulfur are the two most harmful results directly attributable to melting with a reducing atmosphere, there are other indirect results just as harmful which should be considered. When the charge to be melted is made entirely or in part of secondary metal there may be many impurities which, if not removed, will cause defective castings. Small amounts of aluminum and silicon are almost sure to be disastrous. Iron and sulfur are very objectionable. Even phosphorus, so generally used in nonferrous foundries, may cause considerable trouble with high-lead and high-zinc alloys. Such impurities are but slightly affected by melting in a reducing atmosphere, and may greatly aggravate and confuse the results of gas absorption.

On the other hand, a reducing atmosphere may be highly desirable when the metal charge contains considerable metallic oxide. This is particularly true when the oxides are heavier than the resulting alloy. In such a case reduction may proceed over both periods of melting and absorbed gases may be rendered harmless by their action on submerged oxides.

MELTING IN AN OXIDIZING ATMOSPHERE

Turning now to the consideration of melting in an oxidizing atmosphere, we find the first and most serious difficulty to be the formation of oxides in the first period of melting. It is then that the metal charge presents the greatest surface to the action of the furnace flame. Small particles of melted metal dropping downward through the charge may be entirely converted into oxide. In most cases the oxide will rapidly attack the silica of the furnace lining, causing the formation of large amounts of slag and contributing to a heavy metal loss. In the second period this loss by oxidation is not so heavy because the slag formed in the first period serves as a protective layer to the melted metal.

But this process of oxidation, if controlled, can be made to serve a definite and useful purpose. Fortunately the impurities are more readily converted into oxides than are the elements usually desired in bearing bronzes. If these impurities are not present in too great amounts, they may be rendered harmless by selective oxidation. Once converted into oxide, such impurities, being lighter than the metal bath, stay upon the surface and unite with the slag. In addition to this, the excess air of the furnace reduces to a minimum the danger of gas absorption by the

melted metal.   It does this in two ways; first, by greatly reducing the amount of soluble gas in the furnace, and second by reducing the solubility of these gases through the presence of oxide in the melted metal.

The solubility of hydrogen, carbon monoxide and sulfur dioxide in copper is greatly reduced by alloying with tin or with zinc.   It is still further reduced by the presence of oxygen in the metal, the hydrogen and carbon monoxide being oxidized and the metallic oxides reduced. In the case of sulfur dioxide there is no further oxidation but the saturation point of the alloy for this gas is reduced in the same way that tin and zinc reduce the saturation point of hydrogen and carbon monoxide in copper.   The burning of sulfur to sulfur dioxide in the furnace chamber does not render the sulfur of the fuel insoluble in the metal, but the oxygen taken up by the metal as oxide makes the solution of the sulfur more difficult.

It would then appear that a slight amount of oxide in the metal is essential to the production of sound castings from open-flame furnaces when the metal to be melted is of the kind here considered.   Just how the correct amount may be kept present is a question for which no hard and fast rules may be laid down.   It is a matter of adjustment of practice to suit individual furnace installation and metals to be melted.   Oil-fired furnaces as a whole give less trouble from gassed metal than do furnaces fired with gas.   This is because the products of incomplete combustion with oil are largely carbon and carbon monoxide, while with gas, carbon monoxide and hydrogen may both be present.   Hydrogen is much more readily absorbed by the metal than is carbon monoxide—in fact, many believe carbon monoxide to be practically insoluble—so that a fuel containing 50 per cent. free hydrogen is much more dangerous from the point of gassed metal than one containing practically no free hydrogen. The reduction of carbon dioxide to carbon monoxide by carbon is the only source of gas to be encountered in connection with the use of oil, as the possibility of hydrogen by the reduction of water vapor in the usual installations is very small.   However, there is generally much more sulfur in oil than in gas and where metal is to be melted over and over, because of the percentage of gates and turnings produced, this factor may become of considerable importance.

Controlling Gas Absorption, Oxidation and Impurities

In preceding paragraphs it has been pointed out that there is considerably less danger of gas absorption in the first period of melting than in the second.   By the use of a reducing atmosphere in the first period and an oxidizing atmosphere over at least a portion of the second period, the dangers of gas absorption and too severe oxidation may both be eliminated.   The amount of oxygen left in the metal may be controlled

by varying the length of the oxidizing period. In this way, metallic impurities may be removed to a large extent or held at a minimum, and the sulfur content materially decreased.

Through careful analysis of incoming material, and close observation of results assisted by routine physical tests, the adjustment of a satisfactory furnace practice along the lines mentioned should not be a difficult matter.

A careful chemical analysis of incoming material for metallic and nonmetallic impurities is a valuable guide to the extent oxidation may be necessary, or with a standard furnace practice, will determine the amount of dilution consistent with desired results. However, physical tests from metal poured will be the final measures of the correctness of practice. Such tests as strength, elongation and hardness are excellent for the determination of soundness of the material, but as these require special molds and consume considerable time in the making, a simple fracture test is the usual practice where immediate results are necessary. From such a test the extent of shrinkage and absorbed gases, and the presence of impurities such as aluminum and silicon, may be estimated. In connection with a rapid chemical test for sulfur, the results of the fracture test often give sufficient evidence upon which to judge the kind of gas that may be absorbed. For the detection of dross and slag inclusions the rough machining of a casting is almost necessary. Fracture tests in this respect are not satisfactory, as not enough of the sample is exposed by this means for observation.

In connection with this it is interesting to observe that hardly ever will a sample showing gas inclusions be found to contain spots of dross. The one defect is the opposite of the other, just as a reducing atmosphere is the opposite of an oxidizing atmosphere. The condition responsible for visible dross is seldom the cause of absorbed gas.

Summary

Attention is called to the normal chemical actions in open-flame furnaces used in the melting of bronze. Oxidizing, neutral and reducing atmospheres are considered with reference to their effects upon the chemical compositions and physical qualities of the metal melted.

Control of furnace atmosphere, together with close observation of · physical properties as determined by routine laboratory tests, makes possible the production of high-grade castings from classes of raw material frequently considered inferior.

The extent to which refining may be carried economically is dependent on the quality of the raw material, the kind of furnaces used, the nature of the castings to be made and the general foundry layout.

DISCUSSION

H. E. WHITE, Zelienople, Pa.—The question of atmosphere in open-flame furnaces is one which has been given too little attention. It is often the question between the success and failure for this type of melting. Mr. Darby has covered its effect on metals thoroughly in this paper. Neutral atmosphere is much to be desired, but is difficult to obtain. It is assumed that metal melted in crucibles is very nearly under neutral conditions, although this is dependent frequently upon furnace conditions.

Mr. Darby does not speak of the effect of furnace atmosphere on the refractory linings. Because of highly oxidizing conditions metal oxides are formed, such as lead, tin and nickel oxide, which attack silicon carbide linings. These oxides in conjunction with the other oxides of the nonferrous group form active fluxes which attack refractory clay linings and similar super-refractory structures. On the other hand, highly reducing conditions are likely to cause disintegration of refractory clay linings by carbon deposits from carbon monoxide, causing failure similar to those found in blast-furnace linings. The refractory structure is likely to become ruptured and disintegrate rapidly. Recently a chromite lining was ruined by reducing the iron, which is a natural constituent of the chromite.

Undoubtedly the reason why some foundries successfully use silicon carbide linings for open-flame furnaces is atmospheric control. From a metallurgical standpoint it seems logical that the metal contamination so often attributed to silicon carbide is the result of its disintegration by metallic oxides and subsequent absorption by the metal itself, and not direct absorption and disintegration of the silicon carbide by the metal.

Very little silicon contamination was observed when crucible melting was practically the only type in use, although silicon carbide is a constituent of many crucibles.

These assumptions may not hold for melting in electric-arc furnaces, as there seems to be some possibility of dissociation by the electric arc.

O. W. ELLIS, Toronto, Ont.—In the first part of the paper, in discussing the various types of atmosphere that can be present within a furnace of the open-flame type, Mr. Darby does a great service to everyone in calling attention to the fact that is so frequently overlooked, that oxidizing conditions or reducing conditions within the furnace are dependent upon the metal that is being melted within the furnace. A certain mixture of gases can be burning within the furnace and melt one metal, and the conditions within that furnace may be reducing so far as that metal is concerned; on the other hand, with another metal they may be oxidizing.

This is frequently overlooked and the fact that variations in the composition of alloys may actually mean the difference between what Mr. Darby explains here can be oxidizing conditions and reducing conditions is also overlooked.

Mr. Darby referred to the fact that under certain conditions it was possible to get what were defects due to oxidation when the furnace was full, and defects which apparently were due to reduction when the furnace was empty. This raises a question in my mind which has often been brought there when I have been investigating foundry defects, particularly when gas furnaces are being employed. The difference between the gas flame and the oil flame, I think, accounts to a large extent for the difference between the gas furnace and the oil furnace. In a gas furnace when full, the short flame is distinctly oxidizing in character. Empty the furnace somewhat and continue to play the flame on the metal with a view to increasing its temperature, and the length of flame results in reducing conditions within the furnace.

A considerable amount of discussion this afternoon has hovered around the two words, "oxidizing" and "reducing," but so far as I know no one has definitely stated how they knew that conditions within the furnace were oxidizing or reducing. That is just where the crux of the matter lies, and what I want to suggest is that in experi-

mental work of this type we should try to use some test whereby we can determine whether conditions within a furnace are oxidizing or reducing, relative to some particular type of metal.

This may be difficult to do, but might I suggest this as a possible test? Suppose that we take a ladle of material resistant to high temperatures and line it with some suitable refractory material, then place within the ladle a sample of copper and introduce it into the furnace, and after the run has been made examine the copper to see whether it has been oxidized or not. If the sample is left in for a certain definite length of time in every case, it might be possible, by determining the amount by which the sample was oxidized, providing its surface areas was always the same at the top, and provided its volume was constant, to determine how oxidizing conditions were within the furnace.

One could always refer to the effect of the atmosphere upon copper. One need not say that the conditions were oxidizing or that they were reducing, but one could say that the conditions in the furnace were such that within a certain length of time the atmosphere has produced a certain definite proportion of oxide within the copper. I am only putting this forward as an idea. It may be impossible to work it, but it is something that may be of use to investigators on this very interesting subject.

There is just one criticism that I could make, an extremely minute one: I cannot understand how gas is "precipitated." I know what Mr. Darby means, but I think the wrong word has been used. It should be "evolved."

E. R. DARBY.—It is certainly true that we should not judge the atmosphere of the furnace from a sample taken for analysis from any one point. With reference to the illustration given by Mr. Ellis, if a furnace is fired with two burners, one at each end, there may be more or less complete combustion in the center, and there may be complete combustion where the flame is exhausted from the furnace, but where the flame enters the furnace there is not complete combustion, and frequently there is raw gas going over the top of the metal. If this gas is of a kind that is soluble in metal there is no reason why it should not be absorbed at that time, and unless the furnace is continuously agitated I can conceive readily that the metal at the two ends of the furnace may be different in character from that at the center. The center may be oxidized and the two ends may be strongly reduced, or may contain a considerable amount of absorbed gas.

I do not think that enough thought has been given to the proper method of analyzing the atmospheres of open-flame furnaces. I have tried a number of ways to get results as far as analysis is concerned with the metals poured, and I have not yet succeeded. I have tried nearly every method suggested and a good many besides, and I think it would be a very valuable contribution to the furnace practice in general if someone would give us a method of determining the exact composition of the furnace atmosphere where it is in contact with the melted metal.

As regards the word "precipitation," the gas is absorbed, or dissolved, and as the metal decreases in temperature the amount that is held in the solution decreases. Therefore precipitation takes place. It is not evolved, as it is held in the frozen metal.

Recent Developments in Melting and Annealing Non-ferrous Metals

By Robert M. Keeney,* Hartford, Conn.

Important recent developments in the melting and annealing of non-ferrous metals include:

1. Melting of nickel silver in the vertical ring induction furnace.
2. Electric melting of stereotype metal.
3. The rotary-drum gas-fired brass melting furnace.
4. The low-frequency coreless induction furnace.
5. Finishing annealing of brass sheets with city gas[1] replacing wood in the large brass-rolling mill.
6. Electric annealing of brass and copper tubing and sheets.
7. Replacement of oil by gas and electricity in the annealing of nickel-silver shells and stampings.

Melting Nickel Silver in Vertical Ring Induction Furnace

Although over 90 per cent. of the output of the brass rolling mills in the United States is now melted in electric furnaces,[2] until recently a considerable part of the output of nickel silver has been the product of the pit fire.

The application of the electric furnace to the melting of nickel silver has been slow for several reasons: (1) Until recently no lining has been available that gave a satisfactory life in the vertical ring induction furnace when melting nickel silver; (2) the rocking arc furnace so widely used in the foundry does not appear to have been favored by the rolling mill for melting nickel silver, possibly because the gases present may affect the quality of the alloy; and (3) the exclusive rights to the use of the high-frequency coreless induction furnace (which has proved very satisfactory for melting nickel silver) for the wrought brass industry are controlled by one concern.

A little over one year ago the first vertical ring induction furnace to be used for melting nickel silver in the Naugatuck Valley was placed in operation. This was followed by two more in the same mill, and by

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* The Connecticut Light & Power Co.

[1] Unless otherwise specified, the word gas throughout the paper refers to manufactured gas, 530 B.t.u. per cubic foot.

[2] H. W. Gillett: Twenty-five years of Non-ferrous Electrothermics; Fifteen Years of Electric Brass Melting. *Trans.* Amer. Electrochem. Soc. (1927) **51,** 101.

one in a second mill. The results have been so satisfactory both as to improvement of quality of alloy and melting costs that four furnaces are now in operation in the two plants and five more have been purchased. In each plant the electric furnace is replacing the anthracite pit fire.

The melting of nickel silver in the vertical ring induction furnace has involved the development of a suitable refractory lining and a change in the dimensions of the channels. All of the furnaces mentioned are of 75 kw. capacity and pour 400 to 800 lb. per heat with a production of 500 to 550 lb. per hour. The power factor is above 70 per cent. On 24-hr. operation for 6 days per week, the power consumption is 275 to 325 kw-hr. per ton, including holding power used over Sunday. With further experience it is probable that the power consumption will average 275 kw-hr. per ton on the 18 per cent. nickel alloy.

There was considerable difficulty with linings at the beginning of commercial operation, but during a year the lining life has increased from 400 heats to over 800 heats, or about 500,000 lb. per lining. On this basis the cost for lining is $1.40 per ton, and it may be stated with safety that it will not exceed $2 per ton of metal poured.

In comparison with the high-frequency coreless induction furnace, the vertical ring induction furnace not only melts nickel silver with a power consumption approximately 100 kw-hr. per ton lower, which amounts to a saving of $1 to $1.25 per ton, but also has a considerably lower investment cost when installed in small batteries. This differential grows less as the number of furnaces that can be supplied from a single motor-generator set increases. In the small specialty rolling mill this greater simplicity of equipment is of some importance. Both furnaces produce a higher grade metal than the combustion furnace, because the metal is well agitated and is not exposed to the products of combustion. Electrically melted nickel silver is said to roll better than the product of the pit fire. In each furnace the metal loss does not exceed 1 per cent. as compared with 2 to 3 per cent. in the pit furnace.

Most nickel silver mills melt some special alloys in such small quantity as to prohibit the use of the vertical ring induction furnace. The coreless induction furnace is, of course, well adapted to this class of work. The pit fire can be kept in operation at reduced capacity, which is very expensive. In one case a pit fire operating 8 hr. per day consumed 1100 lb. of anthracite coal per ton of nickel silver melted, but in another mill on a 20-hr. day, 700 lb. was used per ton melted. One mill has installed inexpensive gas-fired crucible furnaces for this purpose, and finds the cost of melting with gas at 65 c. per M.c.f. to be about the same as with a battery of pit fires operating at capacity. Silicon carbide has proved to be the most satisfactory lining for the gas crucible furnace.

Table 1 shows typical comparative costs of melting 18 per cent. nickel silver in the pit fire and in the vertical ring induction furnace. The

costs are applicable to an installation melting 10 tons or more per day with 24-hr. operation 6 days per week. Without maintenance and fixed charges included for the pit fire, electric melting is $6 per ton cheaper.

TABLE 1.—*Cost of Melting* 18 *Per Cent. Nickel Silver*

	Anthracite Pit Fire, Per Ton	Vertical Ring Induction Furnace, Per Ton
700 lb. coal at $13 per ton........................	$ 4.55	
290 kw-hr. at 1.15 c.		$ 3.35
Labor (includes all casting-shop labor)............	6.40	3.40
Crucibles.................................	2.00	
Refractories....................................	[a]	1.40
Metal loss:		
Pit fire 3 per cent. or 60 lb. at 7 c..............	4.20	
Electric 1 per cent. or 20 lb. at 7 c..............		1.40
Fixed charges, at 16 per cent....................	[a]	1.55
Total cost per ton........................	$17.15	$11.10

[a] Not available.

ELECTRIC MELTING OF STEREOTYPE METAL

Since the first application of electric heating to melting of stereotype metal in 1925 at Waterbury, Conn., the conversion of fuel-fired pots to electricity has been proceeding rapidly at an increasing rate. Today approximately 19 per cent.[3] of the newspaper circulation of the United States is printed from electrically melted stereotype plates.

In 1927, 4 per cent. was melted electrically, 92 per cent. with gas, 0.6 per cent. with oil and 3.4 per cent. with coal.[4] Eighty-six newspapers in 22 states with a circulation of over 7,000,000, now use the electric stereotype pot. The trend is closely following that of electric linotype melting, which in 1922, after about 5 years of use, accounted for 24 per cent. of the circulation of the country, and in 1927, 57 per cent. In the latter year, gas accounted for 43 per cent.

Most of the electric stereotype pots have a capacity of 1 to 10 tons, and are pots originally designed for gas operation. On the development of an electric immersion heater suitable for immersion in molten stereotype metal, the electric heating of stereotype pots became simple from an engineering viewpoint. The immersion heater consists of a tubular heating element, containing a helical nickel chromium coil surrounded by insulation, around which tubular heating-element iron has been cast to protect it from the moten metal and to provide a suitable surface for

[3] Electrically Heated Stereotype Pots as Load Builders. Industrial Heating Committee, N. E. L. A., September, 1929.

[4] A. M. Apmann. Gas in the Printing Trades. Presented at meeting of Amer. Gas Assn., Atlantic City, N. J., October, 1928.

dissipation of heat. The shape of the immersion heater conforms to that of the pot, with the major part of the heating done by the part lying on the bottom. The heating element extends up the sides to the surface of the metal and from that point terminals go out over the side of the pot. A number of these elements are simply mounted in the pot with their terminals projecting over the top, and the pot is insulated by filling the former combustion chamber, both sides and bottom, with insulating material.

Stereotype metal varies considerably in composition, but the average of five newspapers analyzed: tin, 5.6 per cent.; antimony, 14.1 per cent.; lead, 80.3 per cent. The pouring temperature, depending on the thickness of the plate and the analysis of the metal, is between 550° and 775° F.

The growth of electric melting of stereotype metal has been rapid for a number of reasons:

1. Practically all of the gas pots in use when electric melting was introduced were uninsulated and without automatic control. In the greater number of newspaper offices of this country, under these conditions, electric melting is actually cheaper than gas on a thermal basis. This is obvious when it is understood that for each heat unit consumed in the automatically controlled and insulated electric pot, three heat units must be expended in the uninsulated and hand-controlled gas pot.

2. Under the economic conditions prevailing in the larger newspaper offices—that is, large use of power for presses and linotype machines—electricity is cheaper than the automatically controlled and insulated gas pot on a heat basis only in many cases, and fairly closely competitive in the smaller offices. Insulation of the gas pot reduces the gas consumption by 27 per cent.,[5] and automatic control results in some saving, so that in the modern gas stereotype pot only two heat units must be consumed to produce the result of one electrical heat unit.

3. Improvement of working conditions has been a big factor in the increasing use of electric melting, particularly with the large newspaper. Compared with the prevailing uninsulated gas pot, the electric pot produces a vast improvement in the working conditions of the stereotype room. Even with insulation, the gas pots present other problems such as removal of the products of combustion, especially difficult with the casting room in the basement.

4. From experience up to the present time, it may safely be stated that the maintenance cost of the electric pot is considerably less than that of the gas pot. Pot life has been a problem with gas melting, because of unequal strains set up in the pot when melting cold metal, with the heat applied from the outside instead of from the inside as in the electric pot. During its four years of continuous operation, the maintenance on the first electric stereotype pot, in the office of the Waterbury *Republican-*

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[5] A. M. Apmann: *Op. cit.*

American, has consisted in the replacing of three of its nine elements which burned out during the early period of operation. These were replaced by the manufacturer without charge, as the failures were due to defective manufacture, blowholes in the castings. The cost of a heating element is small, only about $50. The failure of an element in no way affects the publication of the paper, as it can be replaced without a shut down. The pot merely melts a little more slowly while the element is out of service.

5. The cost of electrifying an uninsulated gas pot is little greater than the cost of insulating the gas pot and equipping it with automatic control.

Automatic control is often mentioned as an advantage of electric melting of stereotype metal, but the automatic control of the electric pot produces no results which are not obtained with the automatic control of the insulated gas pot. There may be less lag and more rapid melting in the electric pot, due to the heating being performed entirely in the stereotype metal and not through the pot.

Comparative costs, which are dependable as to their being on a comparable basis, are difficult to obtain. On one newspaper, an 8-ton automatically controlled and insulated gas pot, melting at about the same rate as a 9-ton electric pot consumed 460 cu. ft. of gas[6] per ton melted, with the power consumption of the electric pot, 24 kw.-hr. per ton. On another large newspaper having a 7-ton modern gas pot and a 7-ton electric pot, the gas consumption was 680 cu. ft. per ton[7] and the electric 34 kw.-hr. per ton. In each case, power at 2 c. per kw.-hr. is competitive with gas at $1 per 1000 cu. ft.; or with electricity at 1.5 c. per kw.-hr., possibly about the average of the country for this class of service, the equivalent price for gas is 75 c. per 1000 cubic feet.

ROTARY-DRUM GAS-FIRED BRASS MELTING FURNACE

The electric furnace provided a solution of the melting problems of the brass rolling mill and of the foundry of large and moderate size, with a consequent conservation of a large quantity of fuel and metal, but did nothing for the small brass foundry, where conditions today are about the same as in 1912, when the U. S. Bureau of Mines investigated brass melting. Coke, oil and gas are the prevailing fuels in the small brass foundry with a production of much less than 3000 lb. per day. On such a small production it is very difficult to justify an electric furnace, because it will not earn a satisfactory return on the comparatively large investment required. There are many of these small brass foundries

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[6] A. M. Apmann: *Op. cit.*

[7] Electrically Heated Stereotype Pots as Load Builders. Industrial Heating Committee, N. E. L. A., September, 1929.

in this country, either in the brass-casting business or as an adjunct to large manufacturing plants.

The new rotary-drum gas-fired brass-melting furnace, developed during the past two years under the direction of the Research Committee of the American Gas Assn., appears to fill the requirements of the small brass foundry. The furnace consists of a revolving metallic cylindrical retort, externally fired and enclosed in an insulated steel shell lined with refractory material. The insulated steel shell is mounted on a steel frame so that it can be tilted at any desired angle. Gas burners are mounted on each side in such a manner that they fire into the interior of the lined shell. Within the lined shell is the alloy retort, which revolves when driven by a motor. The temperature of the combustion chamber is controlled automatically.

The first furnace that was built has a capacity of 200 lb. per heat. It has been operated mainly on yellow brass,[3] containing 72 per cent. copper, 1.5 per cent. tin, 1.5 per cent. lead and the remainder zinc, at a temperature of 2150° F. The gas consumption has averaged from 4000 to 5000 cu. ft. per ton in comparison with 8000 to 10,000 cu. ft. per ton in the gas-fired crucible furnace under average conditions, a reduction of 50 per cent. The metal loss has averaged less than 1 per cent., or 20 lb., instead of a loss of 3 per cent., or 60 lb., in the fuel-fired crucible furnace. It is not expected that the metal loss will exceed 1.5 per cent. in foundry operation. The retort has had a life of 500 hr.—about 400 heats of 200 lb. each, or 80,000 lb.

The novel feature of this furnace is the melting of brass in a metallic container. This is possible because the retort is revolved to prevent overheating and nonuniform heating, which would destroy the retort and volatilize the zinc. It is simply the adaption of the rocking or revolving of the arc brass-melting furnace to a combustion furnace and is done for the same reasons.

This novel feature is also the weak point of the furnace, not only with respect to possible contamination of the brass by the alloy of the retort but also as indicated by a study of container costs. The alloy retort is said to result in no contamination of the brass. In the 200-lb. furnace with a retort life of 400 heats, or 40 tons of brass, the retort cost is $4.75 per ton of brass melted. The oil-fired or gas-fired crucible furnace has a crucible life of 35 to 40 heats, resulting in a crucible cost of $2 per ton. The rocking arc furnace, with a lining life of 1500 to 2000 heats, has a lining cost of 40 c. per ton. It is expected that the life of the alloy retort can be increased to 800 heats, which with its present cost still means a retort cost of $2.40 per ton.

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[3] A. Forward: Gas Research Develops Radically New Brass Melting Furnace. *Amer. Gas Assn. Monthly* (May, 1928).

Tables 2 and 3 give a general indication of the field for the rotary-drum gas melting furnace.   Table 2 shows comparative costs for a rolling mill on 24-hr. operation.

TABLE 2.—*Cost of Melting Yellow Brass in the Large Rolling Mill*

	Vertical Ring Induction Furnace, Per Ton	Rotary-drum Gas Furnace, Per Ton
4000 cu. ft. gas at 65 c............................		$ 2.60
Power, 200 kw-hr. at 1.15 c......................	$2.30	
Labor (melting only).............................	1.25	1.25
Refractories......................................	0.40	a
Retort...		4.75
Metal loss:		
Electric, 0.5 per cent., or 10 lb. at 7 c............	0.70	
Gas, 1 per cent., or 20 lb. at 7 c................		1.40
Fixed charges at 16 per cent.....................	0.90	0.90
Total.......................................	$5.55	$10.90

a Not available.

It can be concluded without prejudice that the rotary-drum gas brass-melting furnace can not seriously affect the position of the electric furnace in the large rolling mill, for even if the life of the retort is doubled, and if the gas consumption per ton is reduced materially in the 1000-lb. furnace now being designed, the electric furnace is considerably cheaper. In fact, the retort cost would have to be reduced 50 per cent. and no charge made for gas to compete with the vertical ring induction furnace in the large rolling mill.

The foundry costs shown in Table 3 present a different picture.   These figures are based on a foundry operating a 100-kw. rocking arc furnace of 250 lb. capacity on yellow brass, 10 hr. per day.   The rates for both power and gas have been taken on a marginal basis for the added load. Under the existing conditions for this specific situation, the electric furnace has a considerably lower operating cost on a production of 2 tons per day, but if the life of the retort is doubled as expected, gas is fairly closely competitive with the electric furnace and would undoubtedly show as low a cost as the electric furnace in some situations where the manufacturer might already use large quantities of gas and it could be purchased at a lower marginal cost.

On an output of 1 ton per day, the melting cost in this plant is slightly lower in the gas furnace because the cost of gas does not increase with reduced capacity operation, and because capital charges for gas do not increase with a lower production.   The gas consumption does not increase at reduced output because one furnace is operated at full capacity instead of two furnaces.   The gas rate does not increase because the 24-hr. gas

demand is simply reduced one-half. Capital charges are not increased, because only one furnace is required instead of two.

In the case of the electric furnace, the size installed is already the smallest available, so that it must simply be operated a shorter time. The same 15-min. demand is incurred, so that with fewer kilowatt hours used per month the rate increases. The consumption per ton increases because the furnace is not operating at capacity, and capital charges are doubled.

TABLE 3.—*Cost of Melting Yellow Brass in the Foundry*

	Rocking Arc Furnace		Rotary-drum Gas Furnace	
	2 Tons Per Day, Per Ton	1 Ton Per Day, Per Ton	2 Tons Per Day, Per Ton	1 Ton Per Day, Per Ton
5000 cu. ft. gas at 89 c.....................			$ 4.45	$ 4.45
Power, 300 kw.-hr. at 1.45 c...............	$ 4.35			
Power, 350 kw.-hr. at 2.1 c...............		$ 7.35		
Electrodes, 5 lb. at 23 c..................	1.15	1.15		
Retort.....................................			4.75	4.75
Refractories..............................	0.40	0.40	a	a
Labor (melting only)......................	2.40	4.80	2.40	4.80
Ladle heating............................	0.50	0.50	0.50	0.50
Metal loss, 1 per cent., or 20 lb. at 7 c......	1.40	1.40	1.40	1.40
Investment charges:				
Electric, 16 per cent. on One furnace.........................	1.15	2.30		
Gas, 16 per cent. on Two furnaces......................			1.15	
One furnace...........................				1.15
Total..............................	$11.35	$17.90	$14.65	$17.05

a Not available.

The following general conclusions may be drawn:

1. The use of the rotary-drum gas brass-melting furnace in the brass rolling mill will probably be confined to a few isolated cases where local economic conditions are favorable to gas.

2. In the foundry melting 2000 lb. per day or less, it seems destined to replace other types of combustion furnaces, but for a much larger production the extent of its application in competition with the electric furnace depends largely upon the retort cost per ton of brass melted.

Low-frequency Coreless Induction Furnace

A low-frequency coreless induction furnace has been installed recently in an eastern rolling mill for melting special alloys, which can not be melted in the vertical ring induction furnace because of the varying

mixtures and small quantities involved. Formerly a pit fire was maintained for this purpose. There is, of course, a large field for such a furnace in ferrous metallurgy, but its application to non-ferrous melting would seem to be limited to applications similar to the one mentioned and possibly to melting nickel silver. The two types of coreless induction furnaces, the high-frequency and low-frequency, and possibly the new gas furnace, will probably replace the few fires left in brass rolling mills. The low-frequency coreless induction furnace operates on 60-cycle current at normal shop voltages. Because no frequency conversion equipment is necessary, the furnace has a considerably higher over-all efficiency than the high-frequency furnace, and is said to closely approach that of the vertical ring induction furnace. Static condensers must be installed because the furnace has a low power factor.

FINISHING ANNEALING OF BRASS SHEETS WITH CITY GAS INSTEAD OF WOOD

For several years a number of large brass mills have vigorously conducted investigations directed toward improvement of annealing practice in the final stages of sheet production. These investigations have been more in the direction of improvement of metal surface and uniformity in the final anneal than along the line of a possible reduction in the number of steps in breaking down, rolling or drawing, which might result from greater uniformity of heat distribution and higher accuracy of temperature control. Close temperature control is being sought, but principally in the final anneal. The situation is somewhat similar to that in the manufacture of condenser tubes a number of years ago, when it was realized that season cracking was prevented by a careful final anneal at the proper temperature, and that the last drawing operation and last anneal were sufficient to control the final grain size within the usual tolerances. For the finishing anneal of sheets, electric, gas and oil furnaces have been studied.

A New York state mill has operated electric furnaces fairly successfully for a number of years on the finishing annealing of coiled brass sheets. For two years an electric furnace has been finishing annealing thin sheets in another eastern mill. Within the past year a Chicago mill and a Detroit mill installed electric muffles for the same class of work. Electric furnaces for the annealing of brass tubing and shells in specialty plants steadily increase in number, and it seems that the greater part of this class of work eventually may be performed electrically. The original 350-kw. electric furnace installed in Waterbury in 1923 for annealing tubes, has now operated daily, 10 to 12 hr. for almost 7 years without a coil burn-out or other furnace maintenance expense. The reliability of the electric annealing furnace and of its heating elements has been proved.

Two very important developments of recent months have been:

1. The installation of a large continuous gas-fired annealing furnace for the finishing anneal of coiled sheets, replacing wood, in an eastern mill.

2. The construction of a new rolling mill in the Middle West in which 750 B.t.u. mixed gas is used for all annealing operations. This development is the result of several years of research conducted in cooperation with the Research Committee of the American Gas Assn. with a view to obtaining a bright anneal in a gas furnace. At present there is no commercial method of bright-annealing brass; some oxidation results in the ordinary electric furnace just as in the fuel muffle. The electric water-sealed furnace produces a water-stained brass. The hydrogen anneal gives a dirty gray surface. In the laboratory it was found that when a sheet of clean brass was annealed in an atmosphere of pure nitrogen or some inert gas, a bright anneal resulted, but when the gas used was the purified flue gas from the annealing furnace, results could not always be duplicated. It appears that the failure to secure a bright anneal regularly was caused by liberation of absorbed gases from the metal when heated to annealing temperature; that is, brass is self-tarnishing. To secure a bright anneal, the brass was cleaned of its mill oil. When the problem of cleaning was investigated, the cost of the procedure was found to be so great as to prohibit its use, and the research is now being conducted in other directions. The results to date indicate that brass with mill oil on it can be successfully bright-annealed in a suitable atmosphere in the gas furnace, but a further reduction in the cost of providing this atmosphere must be made to make it a practical process.

In spite of the difficulties encountered, the results were so encouraging that one large continuous gas-fired furnace has been built, replacing wood on the finish anneal. A bright anneal is not being obtained in the production furnace, but the finish of the gas-annealed brass is superior to the product of the wood muffle, as it is understood that the stains sometimes left on the finished pickled sheets after annealing in the wood muffle have been eliminated. With gas improving the finish anneal, an operation for which the wood has always been considered the most satisfactory fuel, replacement of wood by gas in the eastern rolling mill seems only a question of time, because under present local conditions manufactured gas is closely competitive with wood on a thermal basis and because the trend in industrial process heating is increasingly toward the more refined fuels and electricity. The cost of wood is increasing. Five years ago wood was $8 per cord; now it is $10. Also, while a cord of wood is supposed to be a cord of wood, 128 cu. ft., it appears that it is somewhat variable both as to quantity and quality, and the mill possibly does not get full value. On the other hand, the trend of gas rates in eastern rolling mill centers is downward, with marginal gas today 65 c.

per 1000 cu. ft. as compared with 80 c. 5 years ago. Other factors are the cost and inconvenience of handling wood, irregularity of supply, and a growing sentiment among some of the larger mills which own their own timber that the country should be kept beautiful and not despoiled by wholesale cutting of wood.

Tests made in two different mills resulted in a wood consumption of. 0.066 cords per ton of coiled brass sheets, which with wood at $10 per cord at the furnace means a heat cost of 66 c. per ton. It is probable that the gas consumption will not exceed 1200 cu. ft. per ton, so that with marginal gas at 65 c. per 1000 cu. ft. the cost of fuel with gas is 78 c. per ton. When gas or electricity approach as closely as this to the cost of the fuel in use on a heat basis only, the greater uniformity of product, better finish and decrease in rejections usually result in a saving offsetting the higher heat cost. With a possible reduction of gas consumption to less than 1000 cu. ft. per ton in a counterflow furnace, the fuel cost for gas is less than that of wood.

In its present state of development, with no attempt at atmospheric control, the electric brass-annealing furnace apparently does not produce as good a finish in the finishing anneal as either gas or wood. A considerable amount of experimental work with electric heating has led to this conclusion in one mill. The stain that sometimes appears on pickling after annealing with wood or oil is said also to occur after electric annealing. Any dirt on the brass entering the electric annealing furnace tends to bake on considerably more firmly than is the case in the combustion furnace, where dirt and grease oxidize and burn.

On a thermal basis only, electricity is closely competitive with gas under the economic conditions prevailing in eastern rolling mills. The control of its atmosphere is a subject worthy of much study to enable it to meet the requirements of the finishing anneal of the rolling mill. In the specialty shops, these exacting requirements are not encountered, and the question whether electricity or gas should be used is one of over-all costs, depending on the local economic situation.

ELECTRIC ANNEALING OF COPPER TUBING AND SHEETS

Considerable progress has been made in the atmospheric control of electric furnaces for bright-annealing copper. Oil continues to be the fuel of the eastern rolling mill, but electricity is still extending rapidly for annealing seamless tubing, coiled sheets and wire. Continuous electric furnaces of the tube type have been built for bright annealing of copper tubing in an atmosphere of steam or some inert gas. Pit-type electric furnaces of the retort are now in use for bright annealing of coiled copper sheets in an atmosphere of steam. With neither of these two types of furnaces is a water seal used, which results in a much higher output per kilowatt hour—as high as 20 lb. per kw-hr., or 100 kw-hr.

per ton in comparison with 13 lb., or 155 kw-hr. per ton in the most modern water-sealed furnaces, when annealing at a furnace temperature of 1300° F. Cost comparisons between water-sealed electric furnaces and water-sealed fuel furnaces, both of the pit type, show a considerable saving in favor of the electric furnace, due to lower maintenance cost. A properly constructed water-sealed electric furnace has little maintenance expense; two furnaces installed in Waterbury 5 years ago have operated continuously without coil burn-out or other maintenance expense. It would seem, however, that the continuous tube furnace, or the retort type of pit furnace has still greater possibilities of reduction of operating costs.

It is reported that experiments have indicated the possibility of bright-annealing copper in an atmosphere consisting of a mixture of the products of combustion and unburned city gas. The gas furnace will then be considered for annealing in the specialty shops, on which in recent years electric furnaces of the type mentioned have been applied. Even if it produces the same grade of product it is doubtful whether the gas furnace will affect the electric-furnace situation in the specialty shop for two reasons: (1) The shop being already a user of power can add electric load at a considerably lower proportionate rate than it can get for gas when starting its use; (2) the over-all efficiency of the combustion furnace drops off rapidly as the size becomes smaller, while that of the electric furnace remains almost stationary. While a gas furnace treating 3 tons per hour will anneal brass at 1100° to 1200° F. with a gas consumption of 1200 cu. ft. per ton, the gas consumption in a furnace treating 1000 lb. per hour at 1300° F. will probably be not less than 3000 cu. ft. per ton. Under the local economic conditions of some eastern shops, with gas at 85 to 90 c. per 1000 cu. ft. and power at 1.7 c. per kilowatt-hour, the heat cost with each furnace would be as follows: gas $2.38 per ton; water-sealed electric using 155 kw-hr. per ton, $2.63 per ton; and the pit-type electric furnace using 100 kw-hr. per ton, $1.70 per ton.

REPLACEMENT OF OIL BY GAS AND ELECTRICITY FOR ANNEALING NICKEL-SILVER STAMPINGS AND SHELLS

Interesting developments are taking place in the annealing of nickel-silver stampings and shells. For several years electric furnaces have been replacing oil furnaces for annealing stampings, but gas has now actively entered the field, largely because of the introduction of the modern continuous belt furnace, operated with careful control of chamber atmosphere. The gas consumption has been reduced in this furnace to 3000 cu. ft. per ton when annealing at 1400° F. in comparison with 3900 cu. ft. in the pusher type furnace. This reduction of 25 per cent. in gas consumption with a product as clean as that of the electric water-sealed furnaces of both the pit and horizontal types means that in many situations the cost of annealing is less in the gas furnace than in either of the

two types of electric furnaces. The gas furnace can claim all of the pickling savings of the electric furnace, but in each case some pickling is still necessary. Under the stress of competition from the gas industry, the electric-furnace industry has gone two steps farther: (1) in the development of a woven-belt type of continuous electric furnace with a seal of burning city gas on the charging end and a water seal on the discharge; (2) in the application of a hydrogen chamber at the discharge end of an electric furnace of the pusher type. The belt-type electric furnace with the gas and water seals puts the electric furnace on about the same operating cost basis as the belt-type gas furnace, and the production at 1400° F. is about 13 lb. per kilowatt hour or 155 kw-hr. per ton. All four types of furnaces, gas and electric, result in material savings in the annealing of nickel-silver stampings, as compared with the box-type oil furnaces previously used, both in labor and in acid consumption in pickling.

Test made in an electric hydrogen furnace on annealing of nickel-silver stampings resulted in an absolutely clean product, so bright that all pickling can be eliminated. It is expected that the power consumption will not exceed 200 kw-hr. per ton of nickel silver annealed and that the hydrogen consumption will be between 100 and 200 cu. ft. per ton. On this basis over-all production costs, considerably lower than any of the other types of gas or electric furnaces, are indicated as due to possible complete elimination of the pickling. While there will undoubtedly be hesitancy among many factories in considering the hydrogen furnace, it has great possibilities with further development.

In the annealing of nickel-silver shells, electricity has made little headway. Most of this class of annealing has been done in oil or gas furnaces, with a definite tendency at the present time to gas annealing. Gas furnaces are successfully annealing nickel-silver shells for domestic appliance manufacturers with the annealed shell sufficiently bright to require no pickling before the next draw, and the appliance manufacturer calls it bright annealing. It is not, however, the bright anneal desired by the tableware manufacturer. In the past electricity has not been able to produce this so-called bright anneal without a water seal, and has not entered the field of annealing nickel-silver shells to any extent, because the large quantity of water that would be carried by into the chamber of a pit-type water-sealed furnace makes the cost of electric annealing prohibitive. Conditions may change with the further development of the electric hydrogen furnace. Recently a large gas furnace replaced three oil furnaces on annealing nickel-silver shells in the plant of one of the largest manufacturers of plated ware in the country.

SUMMARY

Recent developments in the melting and annealing of non-ferrous metals indicate that it is now generally understood to a greater extent

than ever before that a comparison of costs of sources of heat on a thermal basis mean nothing without a complete investigation of overall costs, the only cost figure that results in profit or loss; that profit or loss does not necessarily result from individual process economy; and that the source of heat best suited to one operation may not fit another. These realizations are resulting in a definite trend toward the increasing use of the more highly refined sources of heat, electricity and gas, in non-ferrous metallurgy.

DISCUSSION

D. K. CRAMPTON, Waterbury, Conn.—Some erroneous impressions might possibly be obtained from statements on pages 423 and 424 of this paper. Strictly bright annealing in pure nitrogen cannot be done. Almost bright annealing is attained, but the result is the same as that in pure hydrogen—a dirty gray surface, which probably is partly due, as the author states, to gases in the metal, but also probably partly due to the volatilization of zinc.

WOOD VERSUS GAS OR ELECTRICITY

Further on there is a statement that a bright anneal is not being obtained in the production furnace, but the finish of gas-annealed brass is superior to the product of the wood muffle. That is not the case. Results equal to wood are obtained, but not superior.

I cannot entirely agree with Mr. Keeney on his figures on cost comparison between wood and gas annealing. In the first place, wood is still $8 a cord, not $10, although I have no means of predicting what it might possibly be in the future. As stated, a cord of wood is not actually 128 cu. ft., but even on the basis of correct information the figures still are decidedly in favor of wood. The actual cost of wood annealing, for comparable conditions, is more than $0.50 per ton of metal and $0.66 per ton of metal, as is given near the top of page 424.

I do not hold any brief for wood annealing—we do not like wood; it is messy and not as capable of accurate control as gas or electricity. With the newer types of annealing furnaces, either for gas or electricity, a great deal of attention is being paid to better engineering design, better efficiencies, and better insulation. A wood muffle could be built today with the same degree of care in engineering, and with the same degree of insulation, which would give a vastly better account of itself than the old-style wood muffles which generally are used for comparison.

About the middle of page 424, Mr. Keeney says: "Any dirt on the brass entering the electric annealing furnace tends to bake on considerably more firmly than is the case in the combustion furnace, where dirt and grease oxidize and burn." One might infer that the atmosphere in the electric furnace is reducing, which is not the case. It is probably neutral or slightly oxidizing. I believe the real explanation is that in the fuel-fired furnace there is what might be termed an active atmosphere. The grease and so forth is burned and carried away, whereas in the electric furnace probably the grease, or whatever may be present, is burned on.

BRIGHT ANNEALING WITH GAS

R. J. COWAN, Toledo, Ohio (written discussion).—As Mr. Keeney has indicated, the Industrial Gas Research Committee of the American Gas Assn. has conducted considerable research in connection with the problem of the bright annealing of brass.

Much of this work has been done in the laboratory of the Surface Combustion Co., Toledo, Ohio. As a result of this research, there has been developed a new method for bright-annealing brass in a gas-fired furnace. The method is being developed to a point that indicates its possibilities in industrial operations. We can say that it is now possible under certain defined conditions to bright-anneal brass in a gas-fired furnace and produce fine results.

Mr. Keeney has called attention again to the effect produced on the metal surface by the gases contained within the metal itself, which have a great effect on the bright annealing. Additional information has been given in a paper by E. G. de Coriolis and the writer at a meeting of the American Chemical Society.[9] Suffice it to say that this fact in itself was one of the greatest obstacles we had to overcome in this work. We have found that it is impossible to overcome this by means of any usual gas atmosphere, even when carefully purified.

Reverting to the fact that brass is self-tarnishing at annealing temperatures, the solution to the problem lies in methods that will counteract this self-tarnishing effect. The difficulty is to incorporate in one operation the expulsion of the occluded gases and remove such gases before too much oxidation has taken place, which will nullify the subsequent step of reduction. We believe that the process we have developed in the laboratory has accomplished, under certain stipulated conditions, this very purpose.

Later we will be prepared to present a paper that will give the details of this operation as well as the vast amount of experimental work leading up to this result. This discussion may be considered as only a sort of footnote to Mr. Keeney's paper, and was prompted especially by his reference to the work of the American Gas Association.

GAS FOR STEREOTYPE MELTING

A. M. APMANN, New York, N. Y. (written discussion).—During the year 1929, a great deal of attention was paid to the use of gas for stereotype melting. The sales resistance of newspaper offices for improved methods had been largely broken down by progressive steps made in melting equipment provided by gas-appliance manufacturers and more particularly by the immersion type of electric melting systems, so that new ideas received ready acceptance.

The problem in the Metropolitan area was attacked from two angles: (1) on papers of which the circulation indicated that they would for a long time continue to use the Junior autoplate casters, manually operated; and (2) on papers whose requirements indicated the adoption of the newly developed automatic plate casters. It was believed that the newspaper offices in the first group could have their requirements well satisfied by proper insulation of the pots, automatic temperature control and external firing of the pots. It was common knowledge that the type of temperature control in use on such pots was unsatisfactory from two standpoints: (1) the temperature drop before the opening of the elements was too great; (2) the large consumption of the burners acting under a single temperature control was so great that the temperature of the metal overshot from the heat in the refractories after the controls had closed. For this reason the equipment adapted to stereotype melting had four-burner nozzles in two groups of two. Two temperature-control instruments were used. One instrument was set for 600° F. and controlled the two outer burners in each of the groups; the other was set for 590° F. and controlled the two inner burners of each group. Atmospheric holding pilots were used to keep the metal at a slowly falling temperature, during the off-peak periods. The theory of this method was that when a few plates were cast only a relatively small amount of heat was needed to melt the

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[9] E. G. de Coriolis and R. J. Cowan: Effect of Atmospheres on the Heat Treatment of Metals. Abst. in *Gas Age-Record* (1929) **64**, 344.

cold metal that was added to replace the plates cast. If the capacity of this equipment was not great enough and the temperature dropped to 590°, the second set of burners was ignited. As the temperature increased, the second set was shut off. The results have borne out the theory. Briefly, 228 plates, weighing 75 lb. each, or a total of 16,600 lb. were cast out of an 8-ton pot, with the temperature remaining always above 590° F. and the second set of burners on only about 40 per cent. of the time. The gas consumption during the hour period did not exceed 2100 cu. ft. The temperature curve of the metal showed that over a casting period of 9 hr., during which the cast was from only a few plates in an hour up to the maximum of 228, the temperature varied between 590° and 610° F.

In attacking the second class of offices, those whose maximum demands were great and whose casting extended over a long period of time, making of great advantage the automatic casting equipment, the application of gas fuel was considered from the standpoint that the heat transfer through the existing cast iron pots was too slow because of the thickness of the pots necessary to support the weight of the metal contained therein. Immersion elements following the design of those elements used in the indirect-fired bake oven were built of welded steel construction to give rapid heat transfer. These elements were supplied with a complete mixture of gas and air by a central mixing plant and delivered to the burners, which were a welded part of the immersion heating elements.

As is usual in any development work, some changes were necessary. The original design called for a burner that would have a throttling control. This was soon found impractical and the burners were replaced by those with a constant burning pilot and a heating flame of larger capacity. Constantly burning pilots were so proportioned that in a period of a 17-hr. shutdown the temperature would drop approximately 100°.

The results of the immersion-type elements have been remarkable. During the holding periods, in which no casting is done, as would be expected, the temperature varied within less than 10°. During the heavy casting periods the temperature varied somewhat more than this, but never more than 30°. The data, which so far are of a preliminary nature, show that in a certain 15-min. period 108 plates, or approximately 63,000 lb. of metal, were cast from the pot with a gas consumption of 540 cu. ft. In a one-day's run, 126,000 lb. of metal were cast from an 8-ton pot with a gas consumption of 19,100 cu. ft.[10] The metal displaced by these elements is very small and the heating capacity and efficiency high. From the standpoint of a newspaper office, the present 8-ton pot, regardless of the type of immersion heating elements used, is not the most economical for the best operation. Casting the heavy runs of the special Saturday or Sunday editions, often 40 to 60 plates, without change of mats, the actual metal capacity of the pot is often turned over in about 40 min. A proper reserve safety factor would indicate the need for a slightly larger pot, so that casting at the normal maximum rate with automatic casters, at least one hour's supply would be carried in the pot.

Additional data are being gathered and at a later date complete information will be given covering the operation of gas-fired immersion-type elements for stereotype melting.

A few operating figures might be of interest. Under New York City rates, gas immersion heating produces a plate for about 1.8 c. The cost using external firing was approximately 1.6 c. per plate. The comparative figure for electricity is 2.75 c. per plate.

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[10] Hot tail pieces, contrary to usual stereotype practice, were not added during the run, which increases the heat input by an amount equivalent to 5 per cent. of the total.

Referring to the reference made in Mr. Keeney's paper to a previous article of my own, the comparative data on heat losses showed that these were 3° lower using properly insulated externally fired pots than the internally heated electric pot.

GAS ROTARY BRASS-MELTING FURNACE

J. F. QUINN, New York, N. Y. (written discussion).—On page 418, Mr. Keeney says: "The electric furnace provided a solution of the melting problems of the brass rolling mill and of the foundry of large and moderate size, with a consequent conservation of a large quantity of fuel and metal but did nothing for the small brass foundry, where conditions today are the same as in 1912, when the U. S. Bureau of Mines investigated brass melting. Coke, oil and gas are the prevailing fuels in the small brass foundry with a production of much less than 3000 lb. per day."

We concede the fact that the electric furnace solved the problem of the brass rolling. mill. I believe that the rotary type of gas brass-melting furnace of today is in its infancy. Who of us can see what development the result of research will bring forth?

The Research Committee of the American Gas Assn., when considering the development of this particular furnace, had in mind that it would take care of production in large and moderate sized brass foundries. I do not agree with Mr. Keeney that the rotary type of gas brass-melting furnace is going to fill the requirements of the small brass foundry, because the initial investment in this type of furnace for the jobbing brass foundry is too high.

The gas-fired crucible melting furnace will answer the needs of the jobbing brass foundry for a long time, for two reasons: (1) The initial investment is low; (2) the variety of alloys melted requires several furnaces.

In speaking of the retort, Mr. Keeney says: "This novel feature is also the weak point of the furnace, not only with respect to possible contamination of the brass by alloy of the retort but also as indicated by study of container costs. The alloy retort is said to result in no contamination of the brass." There are two conflicting thoughts in this statement as to the contamination of the brass by alloys of the retort. This question has been discussed with the best metallurgists in the country. They have assured us that there would be no contamination of alloys to the brass.

We will admit that the retort cost per ton of melted metal is exceptionally high, probably on account of the high cost of manufacture; it will be reduced materially when on a production basis. The maximum charge per retort is 225 lb. The melting time per charge is one hour. The average life of the retort is 500 heat hours. The replacement cost per retort is $190. Therefore the retort cost per ton of metal melted is $3.20, which varies somewhat from the retort cost in Table 2. Likewise, if the loss by oxidation and volatilization, as stated in Table 2, for the electric furnace is 0.5 per cent., or 70 c. per ton of metal melted, the gas costs should be exactly the same—not 1 per cent., or $1.40 per ton.

If in Table 3, we change the figures 5000 cu. ft., to read 4000 cu. ft. of gas at 89 c., it changes columns three and four to read $3.56 instead of $4.45. Likewise, Table 2 indicates that 4000 cu. ft. of gas per ton of metal melted is required. Under Retort Replacement, correct the figures from $4.75 to 3.20; leaving all other charges the same, the sum total in column three will be $12.21 instead of $14.65, and $14.61 in column four instead of $17.05.

I believe that the retort rotary brass-melting furnace thermostatically controlled will be the furnace that the production foundry will use.

C. V. SMITH, New York, N. Y.—In the economic consideration of the rotary brass-melting furnace, the cost of heating a crucible or ladle to carry the molten brass from the furnace to the mold has not been mentioned. This is an item of major importance,

and together with the present retort cost it is sufficiently large to render the development of no commercial value.

Another item not mentioned is the formation of a slag on the inside surface of the retort thick enough to interfere with the transmission of heat through the wall of the retort. This accumulation occurs at such a rate that approximately every 18 to 24 hr. it would be necessary to cool the furnace and to break loose the slag if it were not operated intermittently.

The two attempts to produce a gas-fired brass-melting furnace of special design which have been made within the past few years under the sponsorship of the interests mentioned have been peculiarly unsuccessful because certain principles of brass metallurgy and of brass foundry operation, which are well known to everyone in the brass business, although perhaps not to furnace designers, were neglected.

In the section on finishing annealing of brass sheets with city gas instead of wood, one of the most important points in the operation of the gas furnace referred to has not been brought out; that is, the close control of temper obtainable is due to the continuous principle employed, and not to the use of gas. That same uniformity of control is being met in similar furnaces in which oil and electricity are used as heating mediums.

The brass-mill annealing costs are the first I have ever seen publicly, and there seem to be some inaccuracies. The figures given as a comparison of costs of wood fuel versus gas fuel seem to be based on single-shift operation of wood furnaces as against continuous operation of the gas furnace, which results in a more favorable ratio for the latter than is warranted. Gas will have to be available at considerably lower figures than at present to eastern mills before it will be seriously considered for replacing other fuels for finish annealing.

Nickel silver can be bright-annealed under conditions that will not give good results for brass. This is due to the fact that the film of zinc oxide or carbonate produced on the surface of the nickel silver is of the same color as the metal and can scarcely be seen, whereas brass annealed in a furnace under the same conditions will show up that film   ·
against the yellow background of the brass.

ELECTRIC MELTING OF NICKEL ALLOYS

J. L. FADEN, Boston, Mass. (written discussion).—Nickel-chromium alloys are used in the manufacture of heat-resisting castings, containers, etc. The essential constituents of these alloys are nickel, chromium, silicon, aluminum, carbon and manganese. Electric heat is used in the melting of these alloys in order to maintain the quality and uniformity required and to control the chemical composition with precision. One large plant using electric heat exclusively for the melting of this alloy has an 800-kva., three-phase electric 2-ton furnace of the Heroult type for its main production, and two 150-kva. melting furnaces for special work. A record of one daily run is as follows: Average weight per charge, 1900 lb.; number of heats, 5; total elapsed time, 7 hr.; average kw-hr. per ton 668; approximate pouring temperature, 2850° F.

Electric furnaces are used to some extent in the melting of nickel-copper alloys (monel metal). One concern manufacturing steam specialties such as valves, gages, etc., uses six arc furnaces of 250 lb. capacity in one plant, and one in another plant. These furnaces have been in operation for the past seven years and have given good service.

Over a period of four months, melting an alloy consisting of 90 per cent. monel metal and 10 per cent. tin, the average electrical consumption was 770 kw-hr. per ton. The average weight of heat was 240 lb. The furnaces are run approximately 9 hr. per day.

These furnaces are also used for melting copper-tin alloys containing 88 per cent. copper, 10 per cent. tin and 2 per cent. zinc.

ELECTRIC MELTING OF STEREOTYPE METAL

Mr. Keeney has covered this subject thoroughly. The only additional feature in connection with the use of electric pots for stereotype metal that I should like to emphasize is the fact that, in the average newspaper plant, the demand for melting stereotype metal precedes the press run, as the plates after casting are used on the presses. Consequently, the total electrical demand of the plant is not increased greatly by the use of electric melting. A study of five large newspaper plants using electric melting showed that the original plant demand was increased by an average of only 13 per cent. of the electrical capacity of stereotype pots added. This generally means that the cost of electricity for melting is at a low rate.

One city newspaper having a daily circulation of 300,000 and using two 8-ton electric stereotype metal pots melts 1335 tons of metal per month with an electrical consumption of 20 kw-hr. per 1000 lb. of metal cast.[11]

ELECTRIC VERSUS ROTARY-DRUM GAS FURNACES

As stated in Mr. Keeney's paper, the weak point of the rotary-drum type of gas furnace is the revolving metal retort. On pages 420 and 421 an assumption is made that the average life of retort is 400 heats of 200 lb. each. Records on a rotary-drum gasfired brass-melting furnace which has been in operation in a foundry making plumbers' supplies for a year or so showed the following life: First retort lasted 375 heats; second retort lasted 255 heats; third retort lasted 42 heats; average retort life was 224 heats.

Mr. Keeney states that for 40 tons of brass the retort cost is $4.75 per ton. On this basis the first cost of retort would be $190. The retort cost per ton based on a life of 224 heats would be $8.50. Substituting a retort cost of $8.50 per ton in Table 3 gives a total gas melting cost, as follows: 2 tons per day, $18.40; 1 ton per day, $20.80. Adding cost of $0.40 per ton for refractory, we have 2 tons per day, $18.80; 1 ton per day, $21.20.

Over 500 rocking arc electric furnaces have been installed and their reliability proved. The average lining life is definite. On the other hand, only a few rotary-drum gas furnaces are in operation and the retort life is indefinite; hence cost per ton of metal in gas furnace may run as high as $21 or over.

•Mr. Keeney has discussed the use of the vertical ring induction furnace melting yellow brass. This type of furnace is also used to some extent in the melting of alloys having a composition of approximately 85 per cent. copper, 5 per cent. zinc, 5 per cent. tin and 5 per cent. lead. One such installation, consisting of one furnace, operating on a 9-hr. daily schedule, melts about 7600 lb. per day. The charge consists of a large percentage of scrap. The total melting cost per ton for this furnace is as follows:

	PER TON
Power 370 kw-hr. at 1 c.	$3.70
Labor.	1.94
Refractories	1.32
Metal loss 20 lb. at 7 c.	1.40
Mechanical maintenance.	.18
Fixed charges, 16 per cent.	1.25
	$9.79

[11] J. L. Faden: Electric Stereotype Pots Melt 1000 lb. with 20 kw-hr. *Elec. World* (1930) **95**, 113.

ELECTRIC ANNEALING OF ALUMINUM ALLOYS

Mr. Keeney has discussed in detail the heat treatment of brass and copper. The subject of aluminum alloys is also of interest in view of the rapid growth of the automobile and aviation industries.

The heat treatment of strong aluminum alloys is a notable example of a process where electric heat is one of the best solutions. The temperatures are under 1000° F. yet only a few degrees below the point where the alloys would be ruined by overheating. The maximum properties of the metal are developed within a range of about 10° F., therefore accuracy and temperature control is essential.[12]

One large concern producing aluminum-alloy products such as castings for crank cases, motor-car parts, outboard motor parts and pistons, also forgings for airplane propeller blades, connecting rods and motor parts uses the following electric furnace equipment:

No of Furnaces	Type of Furnace	Electrical Capacity, Kw.
3	Pit (5 ft. dia. by 10 ft. deep).	120 each
1	Aging oven (low temp.)	45
1	Continuous conveyor..	100
1	Car........	300
1	Car........	150

A large eastern aircraft factory is using electric heat for the treatment of duralumin and other aluminum alloys, both cast and wrought. These alloys, when made up into delicate and complex parts such as bulkheads for flying boats, fuel tanks, etc., have a persistent tendency to distortion during heat treatment when treated in the ordinary way, even though the temperature is low, because of the great plasticity of the metal at the quenching temperature.[13]

The specific advantages of electricity for this use are:

1. Close and automatic temperature control available with the electric furnace.

2. Vertical-type furnaces are required and electric heat can be applied to this design satisfactorily.

3. Minimum distortion due to heat treatment.

At this plant two electric furnaces are in use, one designed for the treatment of aircraft parts 10 ft. long and the other for parts up to 25 ft. long. The first furnace is equipped with four separately controlled heating zones and the second with six zones. It is possible for these furnaces to maintain a temperature of 10° plus or minus throughout the heating chamber up to an operating temperature of 1700° F.

ELECTRIC MELTING OF ALUMINUM

A rocking arc electric furnace, in the plant of a concern manufacturing textile machinery, replaced an oil-fired furnace. The metal loss and over-all melting cost per ton have been reduced. The average charge of the furnace consists of 180 lb. of No. 12 aluminum, composed of approximately 65 per cent. ingots and 35 per cent. scrap consisting of gates, chips, etc. The length of heat is 20 min.; the production

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[12] A. H. Vaughan: Electric Heat-treating Furnaces. *Iron Age* (1930) **125**, 357.

[13] H. C. Knerr: Heat Treating of Aircraft Parts. *Iron Age* (1929) **124**, 519.

per day is 2340 lb. The pouring temperature is 1500° F. Most of the castings produced are very light and in thin sections, but some heavy castings are produced. The melting cost per ton (5 hr. per day) is as follows:

	PER TON
Electricity, 660 kw-hr. at 1.3 c	$ 8.58
Metal loss, 2 per cent. at 24 c	9 60
Electrodes, 4½ lb. at $0.24	1.08
Linings	.40
Labor	3.30
Fixed charges, at 16 per cent	2.23
	$25.19

If the furnace were operated 9 hr. per day, the total melting cost per ton would be approximately $22.80, the decrease being due to decrease in electrical consumption as well as reduction of fixed charges.

METAL LOSSES AND MELTING COSTS

H. E. WHITE, Zelienople, Pa. (written discussion).—It is to be regretted that more data are not given in this paper on the lining materials used in the vertical ring induction furnace. This has been the one item that has held back the development of this furnace.

Another item which should be considered and brought to a parity is metal loss. In Table 1 pit fires at 3 per cent. and electrics at 1 per cent. may or may not be calculated on the same basis. With nickel silver 3 per cent. is exceedingly high. Following is a study of metal losses for oil-burning crucible furnaces showing the different divisions of these losses which should be considered. In giving results one is likely to compare experimental data determined on one installation against averages which are perhaps of years duration. The following data were taken over a long period of time for No. 60 oil-fired crucible furnaces.

	RED BRASS	YELLOW BRASS
Volatilization	0.18	0.23
Spillage	0.60	0.70
Skimmings	1.13	3.91
Total loss	1 91	4.86

Concerning the rotary-drum gas-fired furnace, is it possible that this alloy drum will scale and cause metal contamination? Even at the low temperatures of the aluminum melting furnaces some of our largest manufacturers have found it necessary to dispense with iron melting pots because of contamination of the metal with iron scale and absorption of iron by the aluminum.

Compared to the usual losses experienced in open-flame furnaces melting yellow brass, a loss of 1 per cent. in this type of furnace is very low if this is total loss. Volatilization losses alone as high as 3 per cent. are normal for this type of melting.

Table 4 gives a list of melting costs and practice figures. The first set was taken from the Transactions of the American Foundrymen's Assn. and the remaining are from careful industrial surveys made by the A. C. Neilsen Co. in cooperation with several of our more modern large foundries. These surveys were undertaken to determine the truth concerning melting cost and are submitted on this basis. There are other foundry installations which undoubtedly show better figures, but it has not been possible to obtain as accurate costs, and accuracy in these reports has been stressed.

TABLE 4.—*Melting Costs and Practice Figures*

MELTING COSTS

	Cost per Ton of Metal Melted					
	Electric Horizontal Arc Rocking Furnace		Vertical Ring Induction Furnace	No 60 Crucible Furnace Oil-fired	No. 88 Crucible Furnace Oil-fired	Oil-burning Open-flame Furnace
	A	B				
Power and fuel cost ...	$ 8 25	$ 6 03	$ 6.39	$ 4 13	$ 1 62	$15.48
Preheating cost	1 20	1 70	1.70			
Crucibles and ladles .	1 25	1.75	1 75	1.35	1.35	
Furnace maintenance . .	2 60	3.11	0 59	0.62	0 45	2.30
Labor............	2 38	3.30	4 06	2 28	1.99	7.70
Metal loss	7 60	1.44[a]	3 00	0 58[a,b]	6 78	12 00
Total direct foundry costs	23 28	17.33	17.49	8 96	12.19	37.48
Fixed charges and overhead .	2 18	0.98	1 51	0 35	0 17	0.78
Total cost, per ton.	25 46	18 31	19 00	9 31	12.36	38.26

[a] Volatilization losses only.
[b] 0.59 for yellow brass.

PRACTICE FIGURES

Power rate, cents per kilowatt-hour......	2.68–3.20	2 00	2.13			
Oil cost, cents per gallon.....	8			6½	4½	7½
Labor rate, cents per hour....	55–60	45–55	45–55	75	70	60
Metal melted....	Red and yellow brass	Red brass	Yellow brass	75 per cent. red; 25 per cent. yellow	Red brass	Red brass
Plant production, tons per year.....	1200	1200	1400	2200	3300	2000
Size of unit, pounds.	350	350	1000	185	250	500
Volatilization loss at furnace, per cent.....		0.5	1	Red Yellow 0.18 0.23		3
Total metal loss	3			1.91 4.86	2.75	

The modern tilting-type crucible furnace is being rapidly improved and several new types are now on the market, which will reduce these figures still further.

Frequently comparisons are made between crucible melting and other types of melting and it seems that either through ignorance or mercenary motives the old-fashioned coke or coal-pit crucible furnaces are used for comparison against the more modern developments of other types of furnaces. The figures mentioned are rather conclusive in showing the possibilities of economies of crucible melting.

The writer is quite in agreement with the author's summary in that a comparison of cost of sources of heat on a thermal basis means nothing without a complete investigation of over-all cost.

FIXED CARBON FUEL

W. BUEHLER, New York, N. Y. (written discussion).—Recent important developments in the melting and refining of non-ferrous metals should include the Fixed Carbon Fuel Process of the Barrett Co.,[14] whereby non-ferrous metals are melted and refined in direct contact with a special fuel. This fuel is used in a cupola type of

[14] This process and also Fixed Carbon Fuel are covered by U. S. Patent 1650126, Reissue Patent 17347 and pending applications.

furnace and successive charges of metal are placed directly on top of the fuel bed. Excellent results are also being obtained in melting large amounts by filling the furnace to the charging door with alternate charges of metal and fuel.

Fixed Carbon Fuel is extremely hard, has high compressive strength, carries a heavy charge of metal without crushing, and contains very little breeze or dust. Its purity and efficiency are important factors contributing to the success of the process. It analyzes substantially as follows: fixed carbon, 98.5 per cent.; sulfur, 0.4 per cent.; ash, 0.5 per cent.

A bed of from 26 to 36 in. of fuel is maintained, depending on the pouring temperatures required. Successive charges of metal are placed directly on top of the bed of incandescent carbon. As metal is being melted, the bed of fuel will shrink somewhat and it is necessary from time to time to add additional fuel to bring the bed back to the height required.

Low blast is used in melting bronze, copper or scrap. For bronze and copper, a pressure of from $\frac{1}{2}$ to $\frac{3}{4}$ oz. and a volume of only 350 to 375 cu. ft. of air per minute is used. The speed with which the metal is melted and brought down into the reservoir cuts down metal losses. There is a slight stack loss but no oxidation of metal because of the reducing conditions in the melting zone.

Charges of from 500 to 600 lb. of bronze borings and turnings can be melted and secured from the tap hole in from 10 to 12 min., including time required for charging. Ingots of coarse bronze or copper scrap require from 2 to 4 min. longer. Fuel consumption because of the intense heat and swift melting is low, and a fuel ratio of 15 to 1 in volume production is normal. That is, 15 tons of metal can be melted with 1 ton of this fuel, exclusive of the bed of 180 to 225 pounds.

An important feature in connection with this fuel and process is the ability to charge more scrap metal and less virgin metal or composition ingots and still obtain a high-grade metal from the tap hole. This is due to the refining and filtering process, which takes place in the furnace while the metal is passing through the incandescent carbon bed.

In melting secondary or contaminated scrap metals containing impurities such as refractory material, slag, sand, gravel, etc., and up to 2 per cent. of free iron, these impurities go into slag, which rides on top of the molten metal. When melting such contaminated metal, it is necessary to draw off the slag occasionally through the slag hole.

Recoveries vary somewhat with type of metal used. In ingots or heavy scrap of 85–5–5–5 composition, the recovery in volume melting runs from 97.0 to 97.5 per cent., while in fine chips of 85–5–5–5 composition, the recovery is about 96.5 to 97.0 per cent. There is practically no loss of tin or lead while melting, and zinc losses are minimized by the special conditions of the process, particularly the reduced and carefully controlled draft. Such zinc losses as occur are compensated for by adding zinc in the pouring ladle.

Pressure-tight castings have been secured, using only clean chips. Numerous competitive tests along these lines on metals 88–10–2 and 85–5–5–5 show that test bars cast from these alloys have almost invariably shown greater density of metal, no segregation or porosity and, consequently, greater ultimate tensile strength and elongation.

Average cost of melting by this process, under properly controlled operation, should be approximately $5 per ton of metal melted, made up somewhat as follows:

Fuel (only 12 to 1 ratio)	$2.92	Current for blast................	$0.10
Labor (one man 75 c. per hr.). . .	0.75	Preheating pouring ladles........	0 28
Linings (per ton)	0.65	Depreciation at 12 per cent.......	0.12
		Total......................	$4.82

There is practically no wear on the linings above the melting zone. The melting zone is about 36 in. deep and is lined with special-mixture high refractory cast blocks. The shell is protected by a 3-in. brick for insulating purposes and these special blocks lie up against the insulating brick.

The inside diameter of the furnace is about 22½ in. Bringing down a 500-lb. heat every 15 min. results in a melting capacity of 2000 lb. per hour. The furnace occupies a floor space of 44 by 44 inches.

Furnaces for using this fuel have been installed in 20 different types of foundries in the United States and have been particularly successful for red brass, standard bronze and bearing metal.

R. M. KEENEY.—It is apparent that there are two camps, those who look upon it as propaganda and those who view it as a battle of sources of heat or of forms of furnaces. Neither is correct, the paper is simply an attempt to present a general picture of some of the recent developments in melting and annealing of non-ferrous metals, prepared at the request of the Committee on Papers and Publications.

I appreciate the information added by Mr. Crampton and Mr. Smith on the finishing annealing of brass. The wood consumption of 0.066 cords per ton is the average of two furnaces which operate 24 hr. per day. The cost of wood at $10 per cord at the furnace is that given me within the past year by a representative of a concern investigating the use of gas for annealing.

The development of the gas immersion unit for heating stereotype pots, described for the first time by Mr. Apmann, undoubtedly offers great possibilities, as it gives the gas-heated pot essentially the same method of heating as the electric pot—internal heating. The paper was written before information on the gas immersion unit was available. Each stereotype melting application should be considered individually. The electric melting pot should be compared with a modern gas pot, not with an uninsulated, hand-controlled pot. Due consideration should be given to the electrical demand created by electric melting. As stated by Mr. Faden, the use of electric melting increases the electrical demand of the plant very little in the average newspaper plant, because the demand for stereotype melting precedes the press run. This means that power for melting is available at approximately the energy charge in the power rate.

Mr. Quinn, with long experience in brass melting, states that the rotary type of gas brass-melting furnace is in the early stage of development, and feels that it has a considerable future, and I agree with him. Because of its youth, the cost figures for it are presented on a conservative basis, when comparing it with electric-furnace costs established over a considerable period of years. I feel that the place of the rotary-drum gas-fired furnace, in its present stage of development, is in the foundry of moderate size, melting between 2000 and 3000 lb. per day. Below an output of 2000 lb. per day it must compete with the crucible furnace having a much lower installation cost, and above 3000 lb. it gets into the electric furnace field.

The life of the lining of the vertical ring induction furnace when melting nickel silver, mentioned by Mr. White, has been much improved since the data given in this paper were obtained. One plant is now melting over 2,500,000 lb. per lining instead of the 500,000 lb. per lining stated in the paper. The cost of electric melting is said to be considerably lower than shown in Table 1. The anthracite pit-fire costs are from the actual operating results of a comparatively new battery of pit fires.

The cost figures in Table 3 for electric brass melting at an output of 2 tons per day are average costs being obtained in Connecticut brass foundries today. The cost data presented by Mr. White in Table 4 do not seem to be on a comparable basis, and so far as the electric furnace is concerned either are the result of unskilled operation or a misapplication. I have never found in practice any plant having electric melting

costs as high as those shown by Mr. White.   One would hesitate considerably before advocating the installation of an electric furnace with power costing 3 c. per kw-hr. The preheating, ladle, maintenance and metal loss figures given are much higher than those of Connecticut foundries using electric furnaces, and I know of no foundry in Connecticut approaching the oil-crucible melting costs shown in the table.   Columns A and B show two 350-lb. rocking arc furnaces, each melting 1200 tons per year, but fixed charges and overhead for one are double the other, an impossibility if the data are drawn up on a comparable basis.   Crucibles and ladles for pouring from the electric furnace cost more than crucibles for melting in the oil furnace, a condition which would seem very improbable.   Labor costs for electric melting on a 1200-ton per year basis are compared with crucible melting on a production of 3300 tons per year, obviously not a fair comparison.

Melting and Casting Some Gold Alloys

By Edward A. Capillon,* Attleboro, Mass.

THE problem of scrap is probably of greater importance in the pro duction of gold, silver and other precious metal alloys than is the case for base metals and alloys. Remelting of gold and silver scrap in the shop is always a costly process because it involves losses by oxidation of the base metals in the alloy with a consequent increase in the percentage of precious metal. This is most marked in the case of alloys containing the low-boiling and easily oxidized metals zinc and cadmium. Since it is not generally feasible to assay every shop remelt it follows that the possibilities of lost values are large. So-called rolled gold and silver plate is made by soldering or welding the precious metal alloys onto base metal. Such plate when defective must be sent to the refinery to recover the gold and silver values, thereby involving additional expense in the form of refining charges. It is obvious therefore that gold and silver alloy scrap is an important item in manufacturing cost and must be reduced to a minimum. The amount of scrap resulting from poor metal will depend on a number of factors in the manufacturing operations, not least among which is the melting and casting practice. The notes which follow are a summary of experiments performed at various times to determine what variables in melting and casting are influential in the production of sound alloys.

METALS USED IN ALLOYING

Pure gold, that is, gold of 24-kt. value is very much too soft for jewelry purposes and it is therefore always alloyed with other metals to increase its hardness and resistance to wear. For the same reason pure silver is seldom used alone but is alloyed with copper, the standard alloy being sterling silver which contains 92.5 per cent. silver and 7.5 per cent. copper. The metals commonly used for alloying gold are silver, copper, nickel and zinc. In addition to hardening the gold and producing alloys of different karat values the use of these metals makes possible the production of gold alloys of various colors such as yellow, red, green and white. The gold-silver-copper alloys vary in color from light greenish-white through green, yellow and red depending on the relative amounts of the three metals. Green or yellowish-green colored golds

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are also obtained by combining relatively large amounts of zinc (maximum about 18 per cent.) with gold, copper and small amounts of silver. In recent years the so-called white golds have been very popular for jewelry chiefly because of the resemblance to the color of platinum. The bluish-white color of these white golds depends on the presence in the alloy of both nickel and zinc, the former in 14 kt. (58.3 per cent. gold) white golds varying between 12 and 17 per cent. and the latter between 4 and 8 per cent. Some of the white gold alloys on the market contain palladium which increases somewhat the workability and gives a white color more nearly like that of platinum. The high cost of palladium, however, prohibits its extensive use in white gold alloys. Silver, copper, nickel and zinc are the only metals used in large quantities for the production of gold alloys in the jewelry industry. Cadmium is occasionally added to some yellow golds but there does not seem to be any logical basis for its use. Besides, it has the disadvantage of being vaporized at a comparatively low temperature so that much of it is apt to be lost on melting. Some time ago a new gold alloy containing aluminum was introduced on the market. Because of its aluminum content it was supposed to be considerably lighter than the ordinary alloyed golds, thereby enabling jewelers to produce a greater number of articles out of a given weight of alloy than had been previously possible. This alloy however was never a commercial success because of the casting difficulties occasioned by the presence of aluminum. Moreover, the aluminum oxide often present in minute inclusions made the polishing of the alloy a difficult and unsatisfactory process.

As stated in a later section of this paper small amounts of certain impurities may have a very harmful effect on the mechanical properties of gold and its alloys. Fine gold and silver are generally of a high degree of purity, gold from the U. S. Mint assaying 99.98 per cent. or better while ordinary commercial silver will assay 99.9 per cent. To avoid contamination it is important to use only the purest base metals for alloying, such as electrolytic copper, Mond process nickel pellets and Bunker Hill grade 99.99 per cent. zinc. Time and labor can be saved and the chances of error lessened by having on hand a number of different base-metal alloys which can be melted with fine gold in various proportions to produce the color and karat desired. Thus, for white gold an alloy containing copper, nickel and zinc is used while for yellow gold the base alloy is copper and silver, or, copper, silver and zinc. When high temperatures are necessary to melt the base metal and zinc in considerable amount is present, as in the case of the copper-nickel-zinc white golds, the melting should be carried on under a heavy layer of boric acid crystals so as to prevent excessive loss of zinc. For convenience in weighing, the base alloy is granulated by pouring slowly into a tank full of water.

GAS AND ELECTRIC MELTING

Although in most cases gas furnace melting is satisfactory the electric furnace has a distinct advantage from the standpoint of metal losses. Since there is no strong upward draft of gases and the temperature can be easily controlled it is possible to cut down loss of zinc and other volatile metals. This consideration is of prime importance where large amounts of scrap stock are returned to the furnace for remelting as occurs in the manufacture of sheet metal stampings in the jewelry industry.

The author made comparative tests of a 12-kt. white gold alloy melted in an ordinary crucible gas furnace and in an electric furnace of the nonmetallic resistor type. No temperature control or pyrometer was used for the gas furnace melt, the correct pouring heat depending on the judgment of the melter. The melts in the electric furnace were made and cast at 2300° F., this temperature being maintained automatically by an electric controller. The time required for melting is about the same for both methods. Twenty ounce melts of the alloy were made in an uncovered graphite crucible and cast to ingots 2 by 3 by 0.5 in. These ingots were then rolled to strip 0.030 in. thick, cut to small pieces about 0.5 in. wide and then remelted and recast. This procedure was repeated four times, samples being taken of the original melt and of the four remelts. The samples assayed as follows:

	Gold, Gas Furnace Melting, Per Cent.	Gold, Electric Furnace Melting, 2300° F, Maximum, Per Cent.
Original melt..	50 09	49.88
First remelt.	50.28	49.93
Second remelt..	50.41	49 90
Third remelt.....	50 35	49 95
Fourth remelt	50 42	49 94
Increase in gold	0 33	0 06

The electric furnace also makes it possible to melt alloys in a controlled atmosphere. As shown in another part of this paper, sterling silver and gold alloys of high silver content are very susceptible to oxygen. For the purpose of melting in vacuum or in various gases the induction furnace of the high frequency type offers interesting possibilities. The high frequency furnace has the advantage over resistance type furnaces that very high temperatures can be obtained making it possible to use metals which because of high fusing temperatures cannot be melted by any other means.

DEFECTS IN INGOTS

Ingot defects which may cause trouble in the mechanical treatment of the alloy or lead to defective finished stock can be approximately

classified under the following headings; (1) surface defects; (2) weak or porous metal; (3) gas inclusions; (4) metallic impurities, oxides, sulfides, etc.

A superficial inspection of the ingot will reveal surface defects but it is often impossible to determine from the exterior appearance of the ingot whether it is defective due to any of the other three causes listed above. Badly "gassed" ingots will either show no pipe at all or a convex surface at the top, but it is quite possible for an ingot to develop a fairly prominent "pipe" and yet contain enough free gas to show blisters in the final rolled and annealed stock.

Surface Defects

These are apt to result from films of oxide carried over with the stream of metal on pouring. It is therefore necessary that the surface of the metal in the crucible be entirely free of oxides before the metal is poured. This can be readily accomplished by fluxing with boric acid crystals. The acid combines with the oxides to produce an easily fusible slag which can be removed by means of a carbon rod. Copper, zinc and nickel oxides are readily fluxed by boric acid. On the other hand, the oxides of such metals as iron, aluminum, manganese, magnesium and chromium form so readily that it is extremely difficult to obtain satisfactory ingots of gold alloys containing appreciable quantities of these metals. These oxides form as a refractory skin on the melt as soon as the flux is skimmed off. Ingots cast from such melts show a wrinkled surface and deep inclusions where the metal has been unable to break through the tenacious oxide films. Possibly some improved gold alloys might result from the use of such metals as iron and chromium if this problem of oxides could be overcome. With recourse to vacuum melting and casting this would be feasible.

Ingot Proportions

As in any metallic casting the last portion of a gold ingot to solidify contains the bulk of the metallic and gaseous impurities. The majority of the ordinary gold alloys do not form very deep pipes in casting but it has been observed that in a poorly proportioned ingot the top contains "porous" metal which generally pulls apart in the early stages of rolling. By a change in the proportions of the ingot mold, scrap from this source can often be reduced to a minimum. In Figs. 1A and B is sketched the type of broad and short ingot which is conducive to much scrap metal. Fig. 1A illustrates the condition where the metal has been poured at one end of the mold and as indicated by the dotted area the poor metal extends practically from the top to the bottom of the ingot. In Fig. 1B the conditions have been somewhat improved by pouring the metal back and forth from one end of the mold to the other but the amount of scrap will

still be about 30 per cent. The proportions shown in Fig. 1C are much more satisfactory and shearing off the top of the ingot does not involve the scrapping of large amounts of metal.

In a well proportioned ingot the length should be about four times the width. Excessively long ingots, on the other hand, are to be avoided as the metal on pouring is apt to splash against the sides of the mold during the early stage of the pour. An ingot suitable for most gold alloys is 3 in. wide by 12 in. long by 0.6 in. thick and will weigh in 14-kt. white gold about 150 oz. Should it be desired to obtain sheets of large
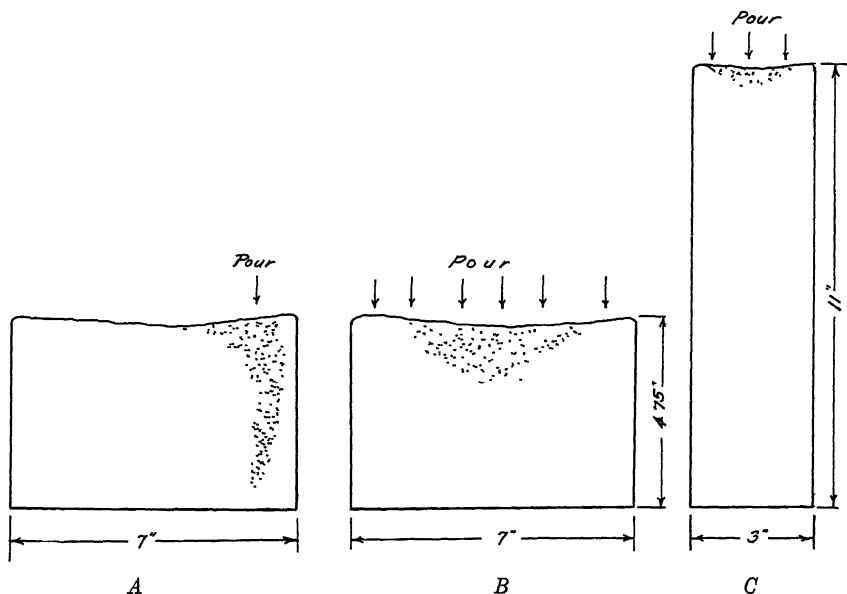
FIG. 1.—A, SKETCH OF POORLY PROPORTIONED INGOT: MELT POURED AT ONE SIDE; DOTTED AREA, POROUS METAL. B, SAME AS A BUT MELT POURED FROM SIDE TO SIDE. C, WELL PROPORTIONED INGOT; POROUS METAL REDUCED TO SMALL DOTTED AREA. Thickness of all three ingots, 0.6 inch.

width as is the case in preparing blanks for long tubes it is best to cross-roll to the desired width rather than cast a wide ingot.

Porous Ingots

It is well known that the solubility of most gases is very much less in the solid than in the liquid metal. Familiar examples are the systems silver-oxygen and copper-sulfur dioxide. When metals solidify in chill molds the bulk of the gas absorbed in melting is liberated but is unable to escape because of the rapidity of freezing of the metal. The result is an ingot which is porous at the center. Such porosity is not generally suspected from the exterior appearance of the casting but if the metal is rolled to thin sheet and annealed the surface will show blisters, their extent depending on the amount of gas retained in the metal when cast.

Blisters may also be caused by inclusions of oxides formed during pouring and mechanically entrapped. These can be largely avoided by clearing the melt with boric acid, as stated in a previous paragraph.

Molten silver absorbs oxygen very readily, one volume of silver at 1783° F. holding in solution 22.4 volumes of oxygen at atmospheric pressure.[1] Solid silver at 1472° F. will only retain 0.354 volume of oxygen, the excess oxygen, about 22 volumes, being liberated on solidification of the metal. The liberation of this large amount of gas causes the well-known "spitting" of fine silver.

Because of this solubility of oxygen in silver, gold alloys containing large amounts of the metal are very apt to absorb oxygen during melting and so form blistered stock. This is not very extensive in alloys containing large amounts of gold as in 18-kt. (75 per cent.) gold, but alloys of gold, silver and copper of 12-kt. (50 per cent.) gold or less do produce blistered sheet in many cases despite the utmost effort to keep a reducing atmosphere in the furnace and to clear the surface of the metal with flux. Carter, in his work on gold-silver-copper alloys,[2] shows that on cold-rolling there is an increase in specific gravity considerably greater than that due to the natural compression of the alloy in the rolling process. For instance, the specific gravity of a 14-kt. alloy containing 58.33 per cent. gold, 20.83 per cent. silver and 20.84 per cent. copper increased from 7.00 Troy oz. per cu. in. for the as-cast alloy to 7.11 Troy oz. per cu. in. for the hard-rolled alloy. The increase in specific gravity is attributed to the presence of gas which compresses more than the alloy itself on rolling.

Melting and casting in vacuum or in inert gases is scientifically the logical method of eliminating gas porosity in cast metals but to date such processes are practical only in the laboratory. The most convenient way of obtaining sound metal in the shop is by the use of deoxidizers added to the melt just prior to pouring. All deoxidizers do not behave alike however and they must be used with much caution as some deoxidizers will often remedy porosity at the expense of hot-short or brittle metal. Deoxidizing agents should have three characteristics, viz., (1) their oxides should form easily fusible slags with flux; (2) they should not form low-melting or brittle compounds with the metal to be deoxidized; (3) their oxides should be insoluble in the liquid metal. Statement 2 is of much importance in considering these materials as small traces left in the metal may often seriously injure its physical properties.

In connection with gold and silver alloys the author has made a number of tests of deoxidizers. The results obtained are summarized below.

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[1] A. Sieverts: The Absorption of Gases by Metals. *Ztsch. für Metallkunde* (1929) **31**, 27.

[2] F. E. Carter: Gold, Silver, Copper Alloys. *Proc. Inst. Metals Div.*, A. I. M. E. (1928) 786.

DEOXIDIZERS

Zinc.—As pointed out by Wise[3] the addition of small amounts of zinc does improve the surface of gold-silver-copper alloy ingots. Zinc, while not a very energetic deoxidizer, has the advantage that in small quantities it does not form brittle compounds with either gold, silver or copper. To check the effect of zinc two melts were made and cast to ingots about 2 by 2 by 0.430 in. Their compositions were:

NUMBER	GOLD, PER CENT.	SILVER, PER CENT.	COPPER, PER CENT.	ZINC, PER CENT.
1	58 3	19.7	22.0	
2	58.3	19 3	21.4	1.0

The surfaces of these ingots were machined down about 0.015 in. on each side and the ingots then rolled to 0.030 in. with reductions of 50 per cent. between annealing at 1300° F. It was found that the annealed strip from ingot 1 was badly blistered while the strip from ingot 2 was practically free of blisters.

Aluminum, Magnesium, Manganese.—These deoxidizing agents have been grouped together because they have one property in common which largely precludes their use in precious-metal alloys. This disadvantage is the fact that the oxides of the three metals form tenacious films on the melt which are not easily fluxed off. The oxides carried over in the stream of metal form deep inclusions in the casting which cannot be removed except by extensive machining of the surfaces.

Silicon.—Tests on an alloy similar to the 14-kt. alloy mentioned under zinc, showed that silicon is quite unsuitable for use as a deoxidizer of gold alloys. While it is true that silicon is a powerful deoxidizer and that it produces melts which are apparently extremely fluid and clear, its use even in small quantities, 0.1 per cent., produces appreciable hot shortness in the alloy, as the following data for an alloy of gold, 58.3 per cent., silver, 19.7 per cent., copper, 22 per cent., show:

Silicon Added, Per Cent.	Effect
0.1	Hot shortness noticeable at 1300° F. in strip 0.020 in. thick
0.25	Alloy brittle as glass at 1300° F. Strip 0.020 in. thick
0.5	Alloy in pasty condition at 1300° F.

The reason for this injurious effect is to be attributed to the formation of a very low-melting gold-silicon eutectic. According to di Capua[4] silicon is practically insoluble in solid gold, the two elements forming

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[3] E. M. Wise: High-strength Gold Alloys for Jewelry and Age-hardening Phenomena in Gold Alloys. *Trans.* A. I. M. E., Inst. Metals Div. (1929) 384.

[4] C. di Capua: The Alloys of Gold and Silicon. *Atti.* Accad. Lincei (1920) I, **29**, 111. Also *Gazz. Chim. Ital.* (1920) 50.

a simple eutectiferous series. The eutectic melts at the remarkably low temperature of 698° F. It follows that the presence of as little as 0.1 per cent. silicon will give rise to this eutectic and so produce hot shortness in the alloy.

Phosphorus.—This nonmetal in the form of copper-phosphorus alloy containing 15 per cent. phosphorus has been found to be a very efficient deoxidizer for sterling silver. It must however be used in as small quantities as possible as any considerable amounts remaining in the alloy will develop hot shortness.

Use of Deoxidizers in Sterling Silver

As has been stated above molten silver has the property of absorbing very large amounts of oxygen, but when the metal solidifies the bulk of this gas is rejected and any silver still in the liquid state is thrown out by the gas with almost explosive force, producing the familiar phenomenon of "spitting." This occurs only in the case of fine silver. In sterling silver the copper, acting in the capacity of a weak deoxidizer, combines with the oxygen to form the stable oxide, Cu_2O. However, not all of the oxygen absorbed by the silver is converted to Cu_2O so that, according to Streicher[5] we are dealing with a four-phase system, namely silver-dissolved oxygen-copper-cuprous oxide. When the silver-copper alloy solidifies the excess oxygen in the silver separates out to form minute pores in the center of the ingot.   These pores produce blisters in annealed strip metal.

Untreated sterling silver when rolled thin, 0.015 in. or less, shows in striking manner the effect of these pores.   Fig. 2 illustrates the appearance of such a strip of silver rolled from an ingot which had been melted in an ordinary gas crucible furnace in contact with air.   The roughness is due to the presence of minute blisters which have broken open in the polishing and also to hard oxide inclusions.   The use of copper-phosphorus has been found very efficient in correcting this trouble.   Fig. 3 shows a flawless silver strip made from silver deoxidized with phosphorus.

Cuprous oxide is readily soluble in liquid copper but the solubility is only 0.009 per cent. in the solid metal,[6] and hence the bulk of the Cu_2O separates out when the copper solidifies.   A similar action occurs when sterling silver containing dissolved Cu_2O is cast.   The presence of this free oxide in the solid alloy produces what Streicher[7] calls "blue" silver. Jewelers have trouble with so-called "fire" in sterling and while in most

[5] S. Streicher: Diseases of Silver (Blistering of Silver, "Blue" Silver and Blister-free Silver). *Ztsch. für. Metallkunde* (1927) 19, 205.

[6] D. Hanson, C. Marryat and G. W. Ford: Investigation of the Effects of Impurities on Copper. Pt. I. The Effects of Oxygen on Copper. *Jnl.* Inst. Metals (1923) **30,** 197.

[7] S. Streicher: *Op. cit.*

cases this is due to superficial oxidation during annealing the author
has found cases in which the "fire" in the stock was the result of oxides
absorbed in the melting process. Ordinary surface oxidation can be
removed by pickling the alloy in acid but oxides originally in the ingot
will not disappear no matter how much the alloy is pickled or polished.
Sterling silver which has been treated with phosphorus is free of this
latter type of "fire" and has a pure white color instead of the bluish-
white color observed in oxide-containing silver.

In connection with this report the author made numerous ductility
tests and chose for this work the Olsen ductility testing machine. This
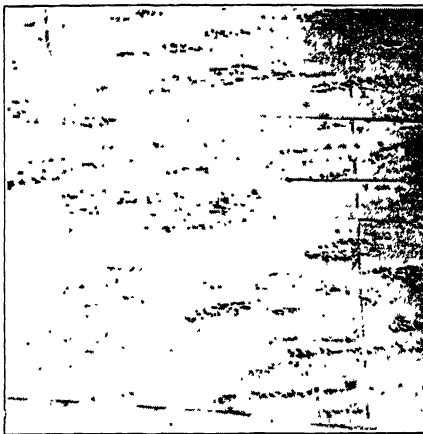
FIG. 2.—ANNEALED STERLING SILVER, NO DEOXIDIZER ADDED TO MELT. UNETCHED. × 75.
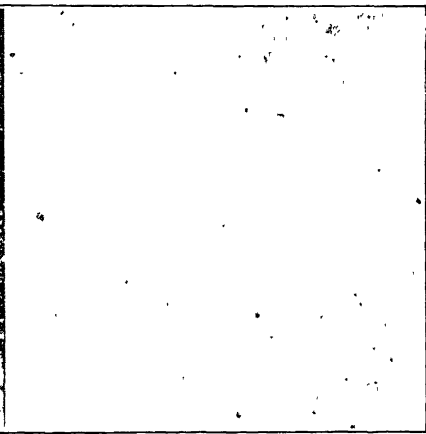
FIG. 3.—SAME AS FIG. 2, BUT DEOXIDIZED WITH COPPER-PHOSPHORUS. UNETCHED. × 75.

ductility test has the advantage that specially shaped specimens are not
necessary and that the quantity of metal required for accurate results is
small, which consideration is of importance in experimenting with
gold alloys.

It is interesting to note that the ductility of sterling silver is appre-
ciably increased by the deoxidation treatment. Similar results have been
obtained for copper by Webster, Christie and Pratt.[8] In some compre-
hensive tests they show that the ductility of phosphorized copper, as
measured by contraction of area, is greater than that of the metal in the
tough pitch condition.

The results obtained by the author for sterling silver (92.5 silver-
7.5 copper) are as follows:

[8] W. R. Webster, J. L. Christie and R. S. Pratt: Some Comparative Properties of Tough-pitch and Phosphorized Copper. *Proc.* Inst. Metals Div., A . I. M. E. (1927), 233.

TEST SPECIMENS: 3 BY 3 BY 0.030 IN., ANNEALED 1200° F.

OLSEN DUCTILITY
DEPTH OF CUP, IN.

Sterling silver, untreated 0.376
Sterling silver, deoxidized with phosphorus...   .. 0 395

Use of Phosphorus in Gold Alloys

As in sterling silver, alloys of gold, silver and copper will contain pores and oxide particles if not deoxidized. Fig. 4 is a photomicrograph of an alloy containing gold, 50 per cent., silver, 10 per cent., and copper, 40 per cent.; a typical red gold of 12-kt. quality. This sample was melted in the gas furnace under oxidizing conditions and shows numerous oxide inclusions. At high power these inclusions appear as bluish-colored
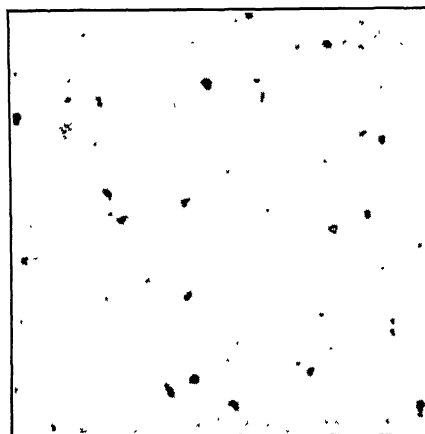
FIG. 4.—GOLD ALLOY (GOLD, 50 PER CENT.; SILVER, 10 PER CENT ; COPPER, 40 PER CENT.) MELTED IN GAS FURNACE, NO DEOXIDIZER ADDED. SECTION OF COLD-ROLLED AND ANNEALED ROD, PERPENDICULAR TO ROLLING DIRECTION. UNETCHED. X 500.

rounded particles, evidently Cu_2O. The presence of this oxide is undesirable as the polished alloy will show a bluish sheen. The action of phosphorus is the same as in sterling silver, the deoxidized alloy being more suitable for highly polished work.

Webster, Christie and Pratt[9] comment on the difference in grain size of cast tough pitch copper as compared to cast phosphorized copper. Precisely the same effect was found in the 12-kt. red gold alloy castings. In the untreated ingot the grain growth is hindered by the precipitation of Cu_2O particles resulting in more or less equiaxed crystals as shown in Fig. 5, while in the phosphorized alloy the crystals grow unrestricted producing the large dendrites of Fig. 6. Both ingots were cast at the same temperature so as to avoid grain size differences due to temperature effects. The large crystals of the phosphorized alloy do not appear to

[9] W. R. Webster, J. L. Christie and R. S. Pratt: *Op. cit.*

cause any difficulty in mechanical working but care must be taken in annealing as the crystals of a deoxidized alloy seem to grow very rapidly above a certain annealing temperature. Large crystals in annealed metal are objectionable as they are the cause of the rough "orange peel" effect noticeable in overheated metal.
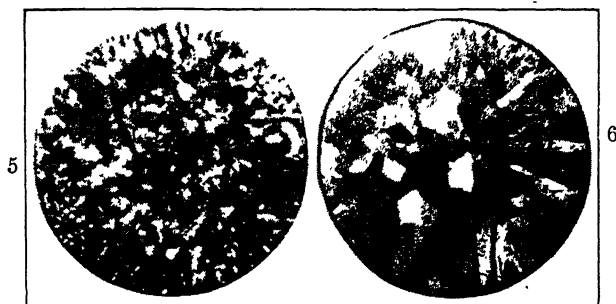
Fig. 5.—SAME ALLOY AS FIG. 4; SECTION OF CYLINDRICAL INGOT. NO DEOXIDIZER ADDED. ETCHED WITH KCN AND $(NH_4)_2S_2O_8$. × 2.5.
Fig. 6.—SAME AS FIG. 5, DEOXIDIZED WITH COPPER-PHOSPHORUS. × 2.5.

Calcium Boride in Gold Alloys

Mention has been made by Wise[10] of the possible use of this material as a deoxidizer in gold alloys. The author conducted several tests with such a deoxidizer containing 85 to 90 per cent. calcium boride, CaB_6, and a few per cent. of carbon, iron and silicon. It is claimed that this deoxidizer is insoluble in copper and copper alloys and therefore any excess can be fluxed off and none will be precipitated in the alloy during solidification. This, of course, is a distinct advantage as too many deoxidizers precipitate harmfully in the solid alloy. Experiments made by the author have proved that calcium boride is very efficient and produces clear melts and good sound castings. Ductility tests on two gold-silver-copper alloys gave substantial increases in favor of the treated alloys, as indicated by the results below.

TESTS SPECIMENS: 3 BY 3 BY 0.030 IN., ANNEALED 1300° F.

Karat	Gold, Per Cent.	Silver, Per Cent.	Copper, Per Cent.	Calcium Boride Added, Per Cent.	Olsen Ductility, Depth of Cup, In.
12	50.0	10 0	40.0		0.329
12	50.0	10.0	40.0	0.15	0.362
14	58.3	19.7	22.0		0.233
14	58.3	19.7	22.0	0.15	0.268

[10] E. M. Wise: *Op. cit.*

CASTING TEMPERATURE

To determine what effect casting temperature might have on the rolling properties and ductility of gold alloys, tests were conducted on two representative alloys, one a 14-kt. white gold, the other a 10-kt.
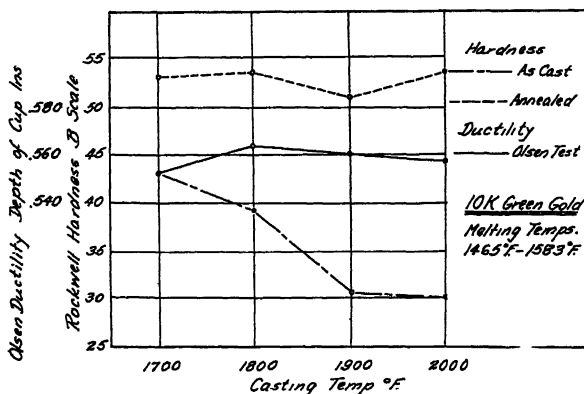
FIG. 7.—EFFECT OF CASTING TEMPERATURE ON HARDNESS OF 10-KT. GREEN GOLD ALLOY, AS CAST. DUCTILITY AND HARDNESS OF ANNEALED ALLOY UNAFFECTED BY CASTING TEMPERATURE.

green gold of the high-zinc, low-silver type. The metals used for alloying were fine U. S. Mint gold, fine silver, electrolytic copper, Bunker Hill grade zinc and Mond nickel. Four melts were made of each alloy, heated to a temperature high enough to insure rapid and thorough alloy-
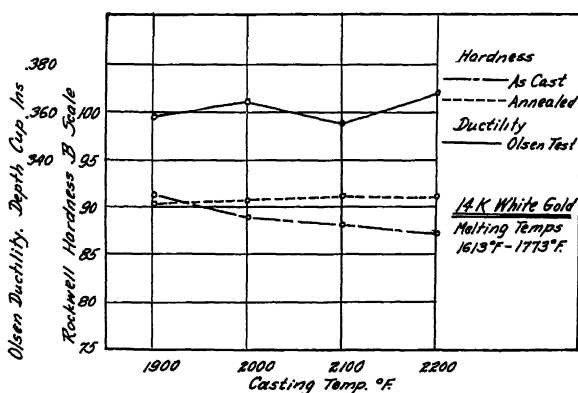
FIG. 8.—EFFECT OF CASTING TEMPERATURE ON HARDNESS OF 14-KT. WHITE GOLD ALLOY, AS CAST. DUCTILITY AND HARDNESS OF ANNEALED ALLOY UNAFFECTED BY CASTING TEMPERATURE.

ing, then cooled to the desired temperature and cast to ingots 2 by 2 by 0.400 in. A liberal amount of boric acid was placed in the graphite crucible to reduce zinc losses. At the high temperatures zinc burned rather vigorously on removing the flux and pouring the melt. Good

ingots were obtained for all casting temperatures except that at the minimum temperature for both white and green gold ingots the surfaces showed "ripples" indicative of rapid solidification. The green gold ingots were cold-rolled to 0.040 in. in three stages with intermediate annealings at 1200° F., while the white gold ingots were similarly rolled to 0.030 in. with annealings at 1300° F. The values obtained for hardness of the cast alloy and for hardness and ductility of the annealed sheet are presented below and plotted in Figs. 7 and 8.

ALLOY, 10-KT. GREEN GOLD
Melting Temperatures, 1465° to 1583° F.
Test specimens, 3 by 3 by 0.040 in., annealed 1200° F.
Maximum Temperature of Melts, 2130° F.

Casting Temperature, ° F.	Rockwell B Hardness, ⅟₁₆-in Ball, 100-Kg. Load		Olsen Ductility, Depth of Cup, In.
	Ingot, as Cast	0.040-in Sheet	
1708	43 1	53 2	0.553
1800	39 4	53 8	0.564
1900	30.7	51 0	0.561
1995	30 1	53 6	0.557

ALLOY, 14-KT. WHITE GOLD
Melting Temperatures, 1613° to 1773° F.
Maximum Temperature of Melts, 2300° F.
Test specimens, 3 by 3 by 0.030 in., annealed 1300° F.

Casting Temperature, ° F	Rockwell B Hardness, ⅟₁₆-in Ball, 100-Kg Load		Olsen Ductility, Depth of Cup, In.
	Ingot, as Cast	0 030-in. Sheet	
1900	90 3	91.3	0.358
2000	88.8	91 6	0.364
2100	88 1	91.2	0.355
2200	87.3	91 0	0.368

It appears from the above figures that the hardness of the alloy, as cast, decreases with increasing casting temperature. This is accompanied by a corresponding increase in grain size as is shown by the photomicrographs of cast cylindrical sections of the 10-kt. alloy, Fig. 9, A to D. The large grain size, except for developing coarsely rough edges on the initial rolling, did not produce any marked difficulties in cold-working. After the first annealing, grain size differences seem practically obliterated. Hardness readings taken of the annealed ductility test samples do not show any marked variations for either alloy. Similarly, the Olsen ductility values do not seem to show any definite

effect attributable to casting temperature, the differences noted being within experimental error.

It appears therefore that for these particular alloys and probably for all other common gold alloys casting temperature has practically no effect on the rolling properties and the ductility of rolled and annealed sheet.

Of course, if an alloy is cast at too low a temperature the metal will solidify before it has a chance to fill out the mold, thereby producing a
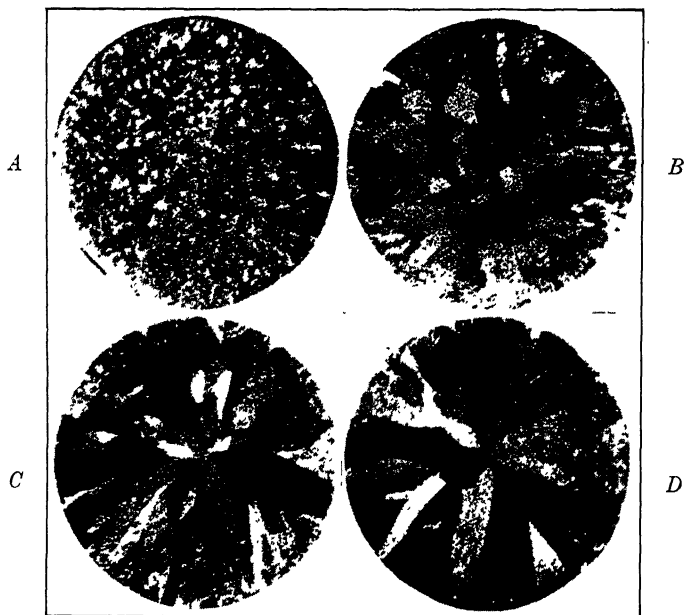
FIG. 9.—SECTIONS OF CYLINDRICAL INGOTS 10-KT. GREEN GOLD ALLOY. CASTING TEMPERATURES: *A*, 1708° F.; *B*, 1800° F.; *C*, 1900° F.; *D*, 1995° F. ETCHED WITH KCN AND $(NH_4)_2S_2O_8$.   × 2.5.

"cold-shut." The alloys should be poured at temperatures from 150° to 250° F. above the liquidus temperature, depending on the size of the melt, casting speed, temperature of the mold, size and proportions of the ingot, etc. On the other hand, excessively high temperatures are undesirable inasmuch as the metal losses due to vaporization of zinc and cadmium will be correspondingly large.

EFFECT OF IMPURITIES

Nowack[11] investigated the effect of small quantities of iron, tin, bismuth, antimony, aluminum, tellurium and lead on the mechanical

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[11] L. Nowack: The Influence of Small Additions of Bi, Pb, Sn, etc., on the Structure and Working Properties of Gold and Gold Alloys. *Ztsch. für Metallkunde* (1927) **19**, 238.

properties of pure gold and 90 per cent. gold-10 per cent. copper alloy. The results he obtained may be summarized briefly as follows:

Iron.—This metal forms a solid solution with gold up to about 15 per cent. iron by weight.[12] Alloys with as much as 10 per cent. iron could be worked without fracturing. An alloy with 1 per cent. iron was as workable as pure gold.

Tin.—A solid solution occurs to about 5 per cent. tin and with larger amounts of tin compounds are formed, such as $AuSn$, $AuSn_2$ and $AuSn_4$.[13] Nowack found that an alloy with 1 per cent. Sn showed a heterogeneous structure even after annealing. The working qualities of this alloy were fair, while an alloy with 0.1 per cent. tin rolled as easily as fine gold. Ten per cent. tin produced an alloy which was very brittle.

Bismuth.—The metal forms a solid solution to about 4 per cent. while alloys with more bismuth consist of solid solution and a eutectic of this constituent and free bismuth.[14] An alloy with 0.1 per cent. bismuth was found to break easily on rolling. One with 0.01 per cent. bismuth could be rolled somewhat further but was still appreciably more brittle than fine gold. Similar results were obtained for the 90 per cent. gold-10 per cent. copper alloy containing bismuth.

Antimony.—A solid solution forms up to about 0.5 per cent. and then a compound $AuSb_2$.[15] An alloy with 0.1 per cent. antimony was found to roll fairly well but with 1.0 per cent. the presence of the compound made the alloy quite unworkable.

Aluminum.—A solid solution appears to exist from 0 to 2.5 per cent. aluminum and then numerous compounds with larger amounts of aluminum.[16] Nowack found that an alloy with 3 per cent. aluminum was practically useless. One with 0.1 per cent. worked readily while with 1 per cent. aluminum fairly good properties resulted

Tellurium.—Nowack found that tellurium affected greatly the working qualities of fine gold. Tellurium is insoluble in gold in the solid state and forms the brittle compound $AuTe_2$.[17] An alloy containing as little as 0.1 per cent. tellurium is unworkable. Only an alloy with 0.01 per cent. or less can be rolled.

Lead.—Like tellurium, lead has an extremely bad effect on gold. The solubility of lead in gold is about 2 per cent.[18] Compounds Au_2Pb and $AuPb_2$ are formed with greater amounts of lead. An alloy with as little

[12] W. Guertler: *Metallographie*, **1**, Pt. 1, 102.

[13] W. Guertler: *Metallographie*, **1**, Pt. 2, 694.

[14] W. Guertler: *Metallographie*, **1**, Pt. 1, 614.

[15] W. Guertler: *Metallographie*, **1**, Pt. 2, 771.

[16] C. T. Heycock and F. H. Neville: Gold Aluminum Alloys. *Phil. Trans. Roy. Soc.* (1900) **194A**, 201.

[17] W. Guertler: *Metallographie*, **1**, Pt. 1, 926.

[18] W. Guertler: *Metallographie*, **1**, Pt. 1, 612.

as 0.06 per cent. lead is unworkable. With a lead content of 0.005 per cent. the alloy can be rolled like fine gold. Nowack tried the effect of annealing on the 0.06 per cent. alloy and found that even after a long period at 650° C. traces of AuPb were still visible and were the cause of the alloy cracking when only slightly strained. Lead has a similar detrimental effect on a 90 per cent. gold-10 per cent. copper alloy, 0.06 per cent. rendering the alloy unworkable.

In an attempt to produce free-cutting low-karat gold alloys for screw machine work the author experimented with alloys containing from 0.5 to 1.5 per cent. lead. While the effect of the lead on the rolling and drawing qualities was not found to be as detrimental as Nowack determined for fine gold, the ductility was nevertheless sufficiently impaired to discourage the use of lead in these alloys. The results obtained with 0.5 per cent. lead are indicated in the following table:

Karat	Gold, Per Cent.	Silver Per Cent.	Copper, Per Cent.	Zinc, Per Cent	Lead, Per Cent.	Rolling Reduction Possible, Per Cent.
8	33 3	10.1	53.3	3 3		Over 78 0
8	33.3	10.0	52 9	3.3	0 5	58.7
12	50.0	9.25	40 75			Over 78 0
12	50.0	9 15	40.35		0 5	56.5

Sulfur in White Gold

In connection with a study of the effect of impurities in gold alloys the author considered it of interest to test the influence of sulfur on the nickel-zinc white gold alloys. These alloys which have been so popular for jewelry in recent years contain from 12 to 18 per cent. nickel depending on the karat value of the alloy. Compared to the colored golds these alloys are quite hard, averaging B 84 to B 93 Rockwell hardness in the "as cast" condition. Because of the presence of large amounts of zinc, 4 to 10 per cent., the white golds are not as subject to gas porosity as are alloys containing no zinc. They do occasionally give trouble in cold-rolling by cracking and splitting. It has been shown by Merica and Waltenberg[19] that of all the elements naturally occurring in cast nickel only sulfur is responsible for the nonmalleability of untreated nickel. These authors state that 0.01 per cent. sulfur in remelted electrolytic nickel is sufficient to render it nonmalleable.

As a test of the effect of sulfur in commercial white gold the author made four 14-kt. white golds containing 0.01, 0.02, 0.05 and 0.1 per cent. sulfur. In addition, an alloy free of sulfur was cast as a check. The alloys were made of electrolytic copper, redistilled zinc, nickel pellets and

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[19] P. D. Merica and R. G. Waltenberg: Malleability and Metallography of Nickel. U. S. Bur. Stds. *Tech. Paper* 281.

fine gold. The sulfur was added to the melts in the form of a nickel-sulfur alloy containing 3.28 per cent. sulfur which was obtained from the International Nickel Co. The ingots were cast about 2 by 2 by 0.430 in. thick and were numbered 1 to 5 from 0 to 0.1 per cent. sulfur, respectively.

Ingot 5 (0.1 per cent. sulfur) split and cracked so badly on the first few passes in the rolls that it had to be scrapped. Ingot 4 (0.05 per cent. sulfur) split from end to end in the plane of rolling after 28 per cent. reduction of area but it was possible to further cold-work after annealing so as to obtain ductility test sheets. Ingot three (0.02 per cent. sulfur) showed some tendency to split but the effect was not as pronounced as in No. 4. Only the ingot with 0.01 per cent. sulfur and the one with no sulfur could be rolled without any difficulty. The samples rolled down for ductility tests were 3 in. square by 0.030 in. thick and were annealed at 1300° F. and air-cooled. These were tested in the Olsen ductility testing machine with the following results:

Alloy No.	Sulfur, Per Cent.	Olsen Ductility, Depth of Cup, In.
1		0.393
2	0.01	0.411
3	0.02	0.397
4	0.05	0.260

From these figures it would appear that as much as 0.02 per cent. sulfur has little influence on the ductility of annealed samples but that in quantity of 0.05 per cent. the ductility is very materially affected.

Examination of the cast sample of alloy 4 showed the sulfur to be distributed as sulfide in a discontinuous network. At high magnification the sulfide is seen to consist of small irregular particles arranged in a structure resembling eutectic. The rolled and annealed alloy shows the sulfide extended in the direction of rolling and apparently present both in the grains and at their boundaries. When annealed at high temperature, such as 1600° F., extensive coalescence of the sulfide particles occurs to form larger rounded particles. The fact that the sulfide does not appear in thin intercrystalline films as in nickel probably accounts in part for the fact that considerably larger amounts of sulfur can be present in white gold than in nickel without seriously affecting the ductility. The effect of sulfur is however sufficiently detrimental to warrant the use of a sulfur-free nickel in the manufacture of white gold alloys. For this purpose Mond nickel of a purity of 99.5 per cent. nickel and higher, containing only small traces of sulfur is the best form of the metal to use.

SUMMARY

1. Defects in gold and silver alloy ingots and their causes have been described.

2. It has been shown that a correctly proportioned mold is necessary in order to obtain ingots which shall give as little scrap metal as possible.

3. Gases in gold and silver alloys produce blisters when the alloy is rolled down and annealed. These gases can be rendered harmless by the use of deoxidizers. The characteristics of various deoxidizers are discussed.

4. In so far as ductility measured by the Olsen test is concerned casting temperature has apparently little effect on the ductility of rolled and annealed sheet.

5. A summary has been given of the effects of various impurities on fine gold. The harmful effect of lead in low-karat. red golds and of sulfur in 14-kt. white gold is shown.

ACKNOWLEDGMENTS

DISCUSSION

T. A. WRIGHT, New York, N. Y.—A point which I do not think was stressed enough was that in regard to scrap. In gold alloys this is extremely important, because we do not measure it in tonnage, but in ounces. The values run so high that inventory control is particularly necessary to avoid a heavy tie-up. Another phase in regard to scrap is that seen in a number of jewelry shops where the melts are about 75 per cent. scrap and 25 per cent. new metal, a situation by no means unusual in such fabricating plants. So that is tied up with the latter part of the paper where Mr. Capillon discusses the effect of impurities.

In reference to the variations of assays in the table on page 441, some of these appear to be but normal assaying errors, and that point should be kept in mind because there is one apparent discrepancy which might cause comment.

Mr. Capillon has gone into the use of calcium boride in gold alloys more deeply than I was able to, but it confirms in general some experiments we did rather crudely some four or five years ago; at the same time, we found about the same results with manganese boride, the purity of which for this purpose was not all that might be desired, as one can imagine.

The author mentions the alloys in which aluminum has been used. Those are patented alloys, and I think that probably the deoxidizer was silicon copper. When the alloys first came out, silicon was not noted in the patents, but silicon was found by analyses in amounts varying with the aluminum and gold. Those alloys seemed to be, as Mr. Capillon says, somewhat in the experimental stage.

With reference to his points about the impurities, I think it is well to stress that which he has mentioned: that these apply primarily to alloys only, but the effect of iron is very important because when alloys give trouble we usually look first to the iron content. If it runs about 0.15 per cent. or over, we take it for granted that the melting has not been as clean as it should be, or that there has been some contamination or other. One should start with a metal of as high purity as possible. The term

"C.P." is used in connection with some of them, but a C.P. label does not always mean what it should, and unfortunately, at times, such a metal is not good enough for some of these alloys.

This too should be noted: I gathered the impression that all the analyses given represent a formula as made up, which is of particular interest in regard to the experiments made with sulfur, as typifying the sulfur presumably added, not the sulfur found in the cast alloy.

E. M. WISE, Bayonne, N. J.—In general I agree with Mr. Capillon in his evaluation of deoxidizers, with some slight exceptions.   I do not believe that manganese is as black as it has been painted.   It does slightly impair the surface of the chill-cast bar, but in spite of this its use is sometimes advantageous.   Silicon, while ordinarily contraindicated in jewelry alloys, does find use in precious-metal alloys used for purposes other than jewelry.   The same remarks apply to phosphorous.   Phosphorous has been used in some of the 14-kt. green gold alloys but its use increases the hot shortness to an undesirable degree.

Mr. Capillon made some reference to the trouble encountered in producing the green gold alloys with high silver content.   Part of the difficulty is due undoubtedly to the high silver content but part is also due to the relatively low melting point inherent in alloys of this color.   One method for avoiding the latter difficulty is to introduce a small percentage of one of the metals of the platinum group.   Palladium perhaps is the most effective in this respect and at its present low price presents attractive possibilities.   The addition of small quantities of palladium also improves the tarnish resistance of the gold alloys.

Monel Metal and Nickel Foundry Practice

By E. S. Wheeler,* Bayonne, N. J.

THE rapid increase in the use of monel metal and malleable nickel in the form of sheet, rod and tube has resulted in a similar increase in the demand for these metals in the form of castings. These castings range in size from small valves and pipe fittings weighing a few ounces to large centrifugal pumps, gate valves and marine propellers, some of the last weighing as much as 24,000 lb. A group of such castings is shown in Fig. 1. A large nickel agitator is shown in Fig. 2.
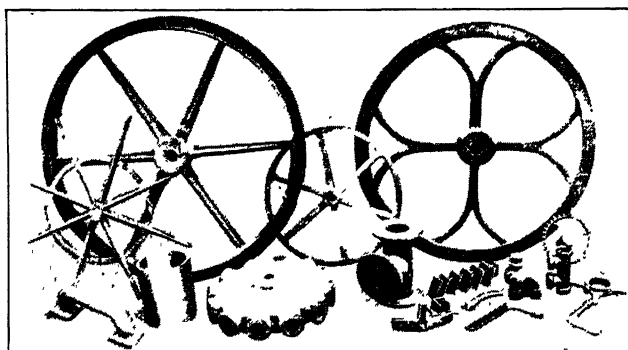
FIG. 1.—A GROUP OF MONEL METAL AND NICKEL CASTINGS.

Monel metal castings are widely used in accessories for steam power plants and in a variety of chemical plant equipment where the corrosion resistance, high strength and toughness characteristic of this metal render it particularly valuable. Nickel castings find extensive use in the construction of corrosion-resistant apparatus, and are often used in conjunction with wrought nickel sheet and tube in the fabrication of equipment for handling a variety of chemical and food products, particularly dairy products.

In response to this demand for castings, numerous foundries have undertaken the production of castings of these metals and have met with varying degrees of success.

The successful production of castings of monel metal and nickel requires careful attention to molding practice, proper melting equipment

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* Superintendent, The International Nickel Co., Inc.

and the application of a definite deoxidizing and desulfurizing treatment. The numerous troubles encountered by foundries in their initial attempts to produce satisfactory castings are due to the lack of appreciation of these essential factors. The object of this paper is to describe the methods used by The International Nickel Co., Inc.; these are the result of experience gained during the past 20 years, in the course of which most of the troubles encountered by the average foundry have been observed and largely eliminated by extensive experimental work.

The shrinkage of both monel metal and nickel is $\frac{1}{4}$ in. to the foot; roughly, twice that of cast iron. This high shrinkage, in conjunction with tenderness slightly below the solidus, characteristic of these metals, necessitates special attention to insure adequate feeding of the casting and special precautions in molding to avoid the production of shrinkage cavities and pulls. The tendency of these metals during melting to absorb gases which

FIG. 2.—A LARGE NICKEL AGITATOR.

later tend to be evolved on solidification renders the problem of the production of sound castings more difficult.

The high pouring temperature required demands the use of a refractory sand, which does not cut or wash away during pouring and thereby become trapped within the casting. Many foundries adequately equipped for melting brass or bronze have made unprofitable attempts to produce castings of monel metal or nickel and usually blame the metal for their failures, whereas the real fault lies in the inadequacy of their equipment.

COMPOSITION OF MONEL METAL AND NICKEL CASTINGS

The chemical compositions of monel metal and nickel castings should closely approximate those given in Table 1.

Manganese is detrimental because it makes the metal sluggish, so that the latter often fails to sharply fill the mold; in addition, it causes the metal to cut the sand, and adds to the susceptibility of the casting to develop pulls or tear .

Sulfur tends to cause the metal to become hot short and in addition renders it brittle at normal temperatures. The behavior of sulfur in monel metal and nickel has been studied by Merica and Waltenberg.[1] It forms the compound Ni_3S_2, which forms a eutectic with nickel that melts at about 630° C. and is very brittle at normal temperatures. Sulfur in the presence of manganese, and particularly magnesium, forms less harmful compounds, but in any case the limit of 0.03 per cent. sulfur should not be exceeded.

TABLE 1.—*Approximate Requirement for Castings*

	Nickel, Pe Cent.	Copper, Per Cent.	Iron, Per Cent.	Silicon, Per Cent	Carbon, Per Cent.	Manganese, Per Cent.	Sulfur, Per Cent.
Monel metal. .	67	28	Under 3.5	0.75–2 0[a]	0.15–0.25	Under 0.50	0.03[b]
Nickel........	Balance		Under 2 0	0 75–2.0[a]	0 15–0.25	Under 0.50	0.03[b]

[a] Depending on the nature of the casting.
[b] Preferably as low as possible.

Silicon, in reasonable quantities, is decidedly beneficial to castings of both monel metal and nickel, because it increases the fluidity of the metal and helps it to sharply fill the mold; also because it reduces the tendency of the metal to cut the sand and partly deoxidizes the alloy. The addition of silicon also increases the physical properties of the resulting casting. A silicon content of 1.50 per cent. is satisfactory for a wide variety of castings. Castings involving a thin web connecting two heavy sections, as in a wheel with a heavy hub and rim connected by thin spokes, are preferably made with a silicon content as low as 0.75 per cent., to avoid the possibility of the development of cracks in the thin section. Very heavy castings may be made of metal containing as much as 2 per cent. silicon.

The addition of a small amount of magnesium is necessary to deoxidize and desulfurize the metal prior to pouring.   The methods for introducing the requisite amount of this metal are discussed below under "Melting."

STRUCTURE AND PROPERTIES OF MONEL METAL CASTINGS

The microstructure typical of cast monel metal is shown in Fig. 3, in which the slightly cored structure characteristic of a rapidly solidified solid solution is evident.

[1] P. D. Merica and R. G. Waltenberg: Malleability and Metallography of Nickel. U. S. Bur. Stds. *Tech. Paper* 281.

The natural corrosion resistance of monel metal in the form of castings is lowered if shrinkage cavities, porosity or foreign inclusions are present. Many cases are on record where the corrosion resistance of monel metal castings has been unsatisfactory entirely because of inferior casting practice employed in foundries not fully conversant with the technique required for producing sound castings of this alloy. A casting may pass rough inspection and still fail to give its full quota of service as a corrosion-resistant material if it is not made according to the best practice.
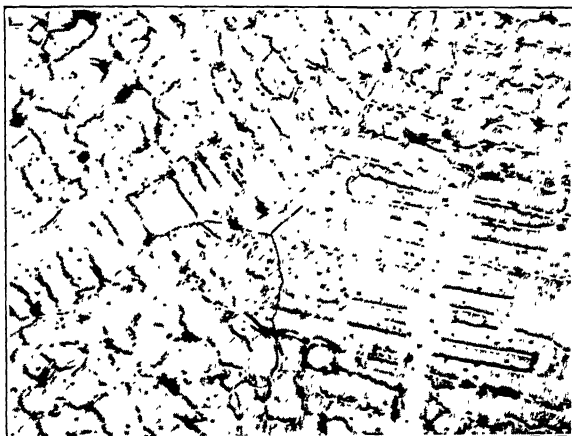
FIG. 3.—THE MICROSTRUCTURE OF A MONEL METAL CASTING.   × 50.
Etched with 60 c.c. nitric acid, 40 c.c. acetic acid, 20 c.c. water.

The excellent physical properties of cast monel metal are evident from the following typical values: Yield point, 35,000 to 40,000 lb. per sq. in.; ultimate strength, 65,000 to 80,000 lb. per sq. in.; elongation, 25 to 35 per cent.

The physical properties of monel metal castings made of metal melted in a basic-lined electric furnace tend to be slightly higher than those of similar metal melted in neutral or acid-lined electric furnaces or crucibles.

MOLDING

The molding of monel metal and nickel castings is similar to that of steel, though no general rule can be given. Risers and sink heads should be placed so that they will feed the casting well and prevent shrinkage cavities. These risers should be placed over the sections where the greatest shrinkage occurs (the heavier ones) and should be large enough to fill these heavy sections properly. As monel metal and nickel chill rapidly, the risers should be large enough so that the metal in them will remain molten as long as necessary to feed the casting properly.

Castings made from patterns having sharp changes in section are subject to considerable trouble from shrinkage and pulling. A chill placed at the heavy section so as to bring its cooling rate to approximately that of the thin section is often beneficial. Large fillets are recommended at all corners. Molds for typical castings would be provided with gates and risers arranged as shown in Fig. 4.

It is advisable to use a minimum amount of binder in the sand, because both monel metal and nickel are sensitive to the gases generated by such binders. An open sand that is highly refractory is necessary, and the molds should be well vented to allow the easy escape of the gases.
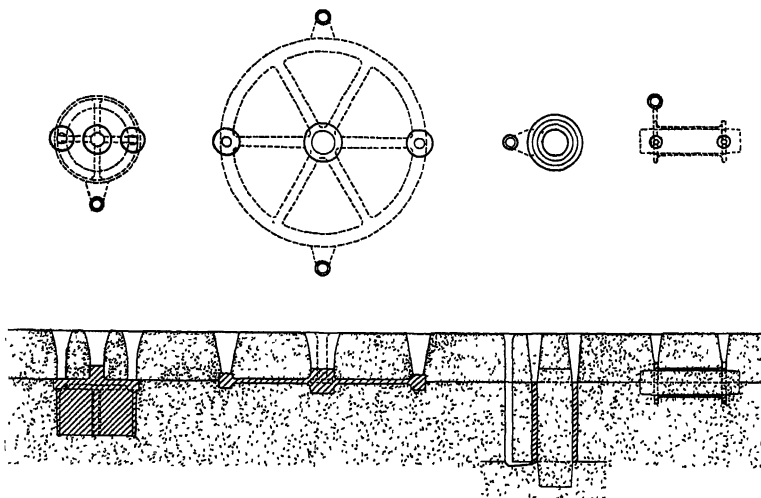
Fig. 4.—Arrangement of gates and risers necessary for production of monel metal and nickel castings.

For light castings (weighing up to 4 lb.), of both monel metal and nickel, a mixture of one part of No. 1 Albany sand, one part of Jersey sand and three parts of old (black) sand is used. This is mixed with either plain water or clay water until the sand is moist enough to stick together when squeezed in the hand. Medium sized castings (weighing from 5 to 20 lb.) are molded in a sand consisting of two parts of old (black) sand and one part of new No. 1 Albany. The sand for heavy castings consists of a mixture of one wheelbarrowful each of Millville gravel, old (black) sand and Lumberton sand, and one shovelful of flour. Water or clay water is added, as for light castings.

Molds for medium weight and heavy castings are well dried before metal is poured into them. Before they are put into the drying oven, they are sprayed with a mixture consisting of equal parts of water and linseed oil and are then coated with a mixture of equal parts of black lead and clay. Light castings may be poured into green-sand molds.

Cores are made of a good grade of silica sand to which pure raw linseed oil is added as a binder. The ordinary proprietary core oils sold under various trade names are unsatisfactory because the large quantity of gas evolved is decidedly harmful to both monel metal and nickel.

The high shrinkage of these metals necessitates the use of soft cores, but these cores must not be so soft that they will crumble or burn when the metal strikes them. Large cores should be hollowed out and filled with cinders or coke, to allow them to collapse easily.

MELTING

Monel metal and nickel can be melted, with good results, in various types of furnaces. Castings are made successfully of metal melted in crucible, open-hearth, single-phase or three-phase electric furnaces. The metal supplied for casting purposes is either in the form of small ingots weighing 5 or 20 lb. or in the form of shot, depending on the requirements of the customer. This material is melted down and just before it is ready to pour the necessary silicon is added. If ingot blocks are used, approximately $1\frac{1}{2}$ lb. of metallic silicon should be added for each 100 lb. of metal. This applies to the majority of castings. If the castings are made by melting shot about $\frac{1}{2}$ lb. of silicon per 100 lb. of metal should be added, as the shot contains initially about 1 per cent. of silicon. The silicon is added about five minutes before pouring and is well stirred in with a wooden pole. Just before pouring $1\frac{1}{2}$ oz. of magnesium per 100 lb. of metal is added. This is used because of its effective desulfurizing and deoxidizing qualities. Stick magnesium only should be used. It is introduced by plunging it well under the surface of the metal with iron tongs, and is then stirred for a few seconds to allow it to diffuse throughout the metal. If the magnesium burns on the surface, no good is derived from it and an additional amount should be added. After the addition of magnesium, the metal is ready to be poured. Pouring should be done as quickly as possible but not so quickly as to prevent the escape of the gases.

Unless electric furnaces are used, low-sulfur fuel oil, containing not over 0.5 per cent. sulfur, is the only fuel recommended. Coal and coke are particularly harmful because of their high sulfur content and no gas furnaces have been found that generate sufficient heat to melt properly either monel metal or nickel. In the oil-fired furnaces no slag is added, the only slag present coming from the crucible or sides of the open-hearth furnace. The same applies to the Detroit electric furnace. In electric furnaces of a type similar to the Moore "Lectromelt," a slag of equal parts of lime and silica sand is thrown on to the bath when the charge is partly melted. The principal purpose for this slag addition is to steady the arc and thereby prevent the continued making and break

ing of the arc. No furnacing other than melting is necessary as the metal as supplied to foundries is of sufficient purity to need no subsequent refining. No additions, except silicon and magnesium, are required.

For most castings monel metal should be poured at a temperature of 2700° F. (1482° C.) to 2750° F. (1510° C.), but for light castings the temperature should be about 2800° F. (1538° C.). Nickel should be somewhat hotter than monel metal, the heavier castings being poured at 2800° F. (1538° C.) to 2850° F. (1566° C.), and the light ones at 2900° F. (1593° C.).

SUMMARY

Monel metal and nickel both being harmfully susceptible to the actions of gases, all possible care should be taken to permit the easy escape of the gases. For the same reason, the use of gas-producing ingredients in molding materials should be reduced to a minimum. Manganese and sulfur are both detrimental, manganese causing the metal to cut the sand badly and causing heavy shrinks while sulfur in excess of 0.030 per cent. makes the metal hot short and brittle. A good grade of refractory molding sand should be used for the molds. Because of their high shrinkage, monel metal and nickel castings are likely to develop shrinks and pulls which often can be overcome by a change of molding practice, the use of heavier fillets, a change of mixture, the elimination of all or part of the scrap used in the charge, or a change in the core when present to permit the casting to solidify without any strain being set up by the excessive hardness of the core. Scrap should be kept down to a minimum and should not exceed 25 per cent. of heavy scrap or 10 per cent. of light scrap. The use of excessive quantities of scrap is frequently responsible for heavy pulls and sometimes causes porosity, by oxidation of the silicon, which is usually present, and the evolution of gas picked up during remelting.

Melting should be accomplished as quickly as possible but not at so fast a rate as to oxidize the metal. In the crucible pits about 2 hr. should be necessary to melt monel metal in crucibles containing 175 lb. of metal, and slightly longer for nickel. This melting rate applies to a hot furnace; obviously, the first melt will require a slightly longer time.

The most important factor necessary for the production of good monel metal or nickel castings is suitable equipment. Without the proper furnaces no amount of good molding or good foundry practice will produce satisfactory castings.

DISCUSSION

W. F. GRAHAM, Mansfield, Ohio.—Mr. Wheeler has performed a useful service in bringing together the various factors affecting the melting and casting of nickel and nickel alloys, as these alloys have proved troublesome to foundrymen accustomed to

handling brass mixtures.   There is, of course, a great deal to be said that Mr. Wheeler did not attempt to cover in his paper.   I should like to mention one viewpoint in relation to the nickel and nickel-alloy casting procedure: For a given alloy, if the melting practice is standardized and religiously adhered to, many of the troubles that occur in the casting of nickel alloys and nickel can be eliminated, and it is not necessary to go to the lengths that a great many foundrymen do in making additions in large quantities of deoxidizing agents in order to obtain relatively sound metal.   These large additions change the character of the material materially and the possibilities of its ultimate service.

Furthermore, this consideration will also more or less nullify one statement that Mr. Wheeler has made in his conclusion regarding keeping down the scrap charge.   I believe that if the melting procedure has been determined definitely for an alloy and adhered to, a remarkable amount of scrap can be used over and over again.   In other words, if the metal has not been contaminated, the original metal remains.

Effects of Cold Working on Physical Properties of Metals

By R. L. Templin,* New Kensington, Pa.

In treating a cast metal by any working process such as rolling, drawing or forging, variations in the conditions present in the remelting, casting, chilling and preheating of the initial ingot will certainly have some effect on the physical properties of the final product. In considering the effects of cold working on the physical properties of metals, however, it will be assumed that these factors, being controlled according to best practice, will remain constant and therefore may be neglected.

Starting with such a uniform metal ingot, the next operation in the production of wrought metal involves hot working by rolling, forging or extrusion so as to produce a slab, billet or bloom. This working must be sufficient to produce substantial grain refinement and minimize any defects occurring in the initial ingot. Even such a hot-worked product is not suitable as a starting material for determining the effects of cold working because it contains internal strains analogous to those resulting from cold working. It is necessary, therefore, to supplement the hot working with a considerable amount of cold working, followed by a proper annealing in order to obtain a material suitable for use in defining the effects of cold working on the physical properties of a metal. That is, if the effects of cold working are to be evaluated accurately it is necessary to have other effects at least constant if not absent. Such material, unfortunately, cannot always be obtained in commercial practice but the requirements just indicated certainly represent the desired goal; this goal has been attained in the treatment of some metals, one being aluminum.

Factors That Must Be Considered Simultaneously with Cold Working

So many other factors affect the physical properties of a metal that it is necessary to consider these factors simultaneously with cold working; their effects vary in magnitude with the amount of cold work present. The most important of these factors are: (1) chemical composition, (2) structure, (3) temperature of working, (4) character of working, (5) rate of working, and (6) methods used for measuring results. For

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* Aluminum Co. of America.

example, when only a small amount of cold work has been done, the physical properties of the metal may be affected more by variations in chemical composition, grain size or structure than by the amount of cold work.

The physical properties of a metal may be expected to vary with the chemical composition of the material; that is, the amount of alloying constituents present. This, of course, is one of the main reasons for the manufacture of alloys. The amount of variation in the physical properties, however, will depend first upon the given nominal composition of the metal, then upon the commercial variations from the nominal composition. For example, we might expect a given set of physical properties to obtain in the case of a 70:30 brass and yet another set of mechanical properties from a 60:40 brass. Slight departures from these compositions would be expected to cause some variation in the physical properties. When the variations in the physical properties due to comparatively small variations in the chemical constituents are appreciable, it becomes necessary to give them consideration in determining the relationships that exist between the cold working and the physical properties of the material.

Under the general topic of "structure" of a wrought metal, consideration must be given to the size, shape and direction of grains. In the absence of cold work, the grain size of a metal becomes of considerable importance. Experimentally it has been demonstrated that a piece of commercially pure aluminum sheet could be cut in half and each half annealed so as to produce in one a very fine-grained structure and in the other a very coarse-grained structure; with the result that the fine-grained piece has a tensile strength about 40 per cent. greater than the coarse-grained piece. This same fact has been observed, qualitatively at least, in the cases of numerous other metals, and merely serves to emphasize the importance of crystal size in wrought metals. A wrought metal that has been rolled or drawn from material having a coarse-grained structure usually contains elongated grains or fibers, which in turn cause the final product to have directional properties with respect to the direction of rolling or drawing, even after final annealing. While directional properties in a wrought product are often the result of an elongated crystal or fiber structure, such properties may be the direct result of certain amounts of cold work given to an equiaxed fine-grained structure. In general, however, a fine-grained wrought metal with equiaxed crystals, which has been annealed or hard worked, exhibits but slight differences, if any, in its mechanical properties, irrespective of the direction of testing.

The temperature at which the working of a metal is carried out affects appreciably the physical properties obtained. Any rigorous study of the laws defining the relationships existing between working

and the mechanical properties of metals must therefore give proper consideration to the temperatures involved. The inclusion of the effect of temperature in the relationships to be defined later would further complicate the problem, however, and since various tempers of many of the metals are the result of cold working at room temperature only, the details of the problem when other temperatures are involved will be omitted from the present discussion. In passing it may be pointed out that when commercially pure aluminum is worked at a temperature of about 200° F. the effect on the tensile strength of the metal, for instance, is only about one-half as great as when the same amount of working is done at room temperature.

Working of a given metal at room temperature may have effects on its mechanical properties that are similar to those caused in another metal worked at a different temperature; that is, what we shall define as cold working for one metal may correspond to hot working for another metal, such as lead or tin.

The character of the work done on metals appears to have comparatively little effect on the final mechanical properties obtained; that is, provided the rate of reduction is the same and the temperature of the material remains within the limits to be indicated, a given amount of reduction by either rolling, drawing, or forging will give the metal the same final mechanical properties. This has been verified by considerable experimental work on one or two metals and many data have been obtained from routine tests of commercial products of aluminum fabricated by the processes indicated.

The rate of working or rate of reduction per pass, draw or blow, on the other hand, may cause some variation in the mechanical properties of a metal. Products that are reduced in area 30 to 40 per cent. per operation frequently exhibit differences in their mechanical properties when compared with similar products that have been reduced in area 5 to 10 per cent. per operation. In general, the product that is worked at the higher rates has more nearly uniform mechanical properties throughout its cross-section than the product worked at the lower rates. In the first case the working is analogous to an upsetting action while in the second it is more like a riveting action. It should be appreciated, however, that the rates of reduction used in fabricating the various metal products are often governed by the class or kind of product, the limitations of the rolling mill or draw bench, dimension tolerances, finish, etc.

The effects resulting from cold-working a metal are usually evaluated in terms of such mechanical properties as tensile strength, elongation, yield point and hardness. Starting with properly annealed wrought metal free from cold work, there is a definite set of mechanical properties which may be anticipated for any given subsequent amount of cold work. Therefore, once the relationships between cold working and

the mechanical properties are known for a metal, theoretically it is necessary to know but one of the mechanical property values in order to indicate the others. Practically, however, the rates of change in the various mechanical properties with respect to cold working are not constant throughout the possible range of cold working, with the result that certain limitations are imposed. Still other limitations hindering the prediction of all the mechanical properties from one known property value and a given amount of cold work are due to shape and size of test specimens, testing procedure and accuracy of test measurements. For example, the Brinell hardness of a wrought metal is used to determine the tensile strength value. For wrought aluminum, the tensile strength is approximately 575 times the Brinell value (based on the use of a 10-mm. dia. ball under a 500-kg. load), or vice versa the Brinell hardness is $\frac{1}{575}$ of the tensile strength value; therefore any errors in the Brinell hardness determination would be multiplied by 575 in arriving at the tensile value. On the other hand, dividing the tensile strength by 575 will give a Brinell hardness value for wrought aluminum that is about as accurate as the value can be determined by actual test.

In addition to the usual mechanical property values, definite relationships have been shown to exist between cold work and the electrical conductivity or resistivity and density of metals. Because these relationships are not of specific import in most cases, they will not be considered in the present discussion. It may be mentioned, however, that the cold working of annealed wrought aluminum, as in the case of other metals, *decreases* its density as well as its electrical conductivity and a slight decrease would be expected in its thermal conductivity.

DEFINITION OF COLD WORK AND EQUIVALENT COLD WORK

In order that the effects of cold working on the physical properties of a metal may be properly evaluated it is necessary to have a suitable definition of what is meant by cold work, as well as a suitable quantitative measure of the cold working. In the discussion which follows, cold working will be understood to mean the reduction in cross-sectional area of the metal which occurs as a result of rolling, forging, drawing or extrusion, at temperatures in the neighborhood of room temperature, that is 60° to 80° F. The change in cross-sectional area of the metal effected by the various processes indicated will in most cases amount to a *reduction* in area of the material, but in special cases, such as upsetting of a billet by forging, the change may amount to an *increase* in the cross-sectional area of the product. Again, in the rolling of wide sheet the reduction in cross-sectional area of the product may without sensible error be considered as resulting solely from the reduction in thickness of the product, since such sheet does not increase appreciably in width during the rolling operation.

When a metal is worked at temperatures above room temperature the effects of cold working are usually less in proportion to the amount of working done than when the material is worked at room temperature. Similarly the working done on metals at temperatures lower than room temperature becomes more effective than the same amount of work at room temperature. It has been found possible, at least in some instances, to evaluate the effects of working at temperatures either above or below what has been defined as room temperature, in terms of what would have occurred had the metal been worked at room temperature. That is, the amount of cold working done at temperatures above or below the range previously indicated may be evaluated in terms of cold working as just defined and termed "equivalent cold working."

An example of the usefulness of such procedure is the case of a hot mill slab which possesses certain mechanical properties as a result of the hot work done upon it, which are not in agreement with similar properties of properly and fully annealed material. These differences may then be considered as resulting from a certain amount of equivalent cold working of the hot mill slab and if the relationship between cold working and the mechanical properties are known for the material in question, together with the dimensions of the annealed hot mill slab, we could readily compute the cross-sectional area or size of the annealed product which if cold-rolled to the dimensions of the given hot mill slab would have the same mechanical properties. Furthermore, we could quite accurately predict the mechanical properties of any harder temper product cold-rolled from the hot mill slab.

With cold working defined as the reduction in cross-sectional area of a product at or about 70° F., it becomes desirable to select a suitable quantitative measure for the amount of cold working done in order that the relationships between cold work and the physical properties of a metal may be properly defined. The problem presented will be appreciably simplified and yet made more general in its solution if the reduction in cross-sectional area is expressed as a percentage change from the initial area. Expressed as an equation this becomes:

$$C = \frac{A - a}{A} \times 100$$

wherein C = amount of cold working in per cent.

A = initial area of the material in the properly annealed condition,

a = area of the cold-worked material.

In the case of sheet metal, where the reduction in area is almost entirely at the expense of thickness, the equation above may be written

$$C = \frac{T - t}{T} \times 100$$

EFFECTS OF COLD WORKING ON PHYSICAL PROPERTIES OF METALS

In order that the effects of cold working on the physical properties of a metal may be adequately defined, it would seem only proper to consider the changes in the properties as percentage variations from the values obtaining in the absence of cold working. This procedure involves one rather serious difficulty; that is, the obtaining of properly annealed wrought metal free from cold-working strains and of the desired structure. This may be better appreciated when we consider the effect of annealing on the tensile strength of a metal such as brass, copper or aluminum. Under various conditions of time and temperature the tensile strength of these metals in the hard wrought condition decreases rapidly to a point where the cold-working strains are nearly all removed. Under higher temperatures, longer time, or both, further decrease in the tensile strength may occur but such further decrease is usually considerably less in magnitude and frequently is the result of crystal growth in the material. In the investigation made by Bassett and Davis[1] the major decrease in the tensile strength of electrolytic copper began at about 200° C. and was followed by a gradual decrease for temperatures in excess of about 225° C. For the lake copper, the major decrease in tensile strength occurred at about 350° C. and was followed by a slight decrease for temperatures in excess of about 400° C. Results similar to those found for the lake copper were found for the sheet brass.

Unfortunately, the material which we wish to use as a starting point in determining the relationships existing between working and the physical properties must come from in or near the transition range, where the tensile strength has just undergone a marked decrease, the elongation an appreciable increase, and crystal growth has just started. That is, the effects of cold working have hardly been removed from a wrought metal before its physical properties are being modified by other factors such as grain size. In order then to obtain a satisfactory set of physical properties for a given metal in the properly annealed condition it becomes necessary to consider physical property values obtained from large numbers of tests of such material.

Since the tensile strength of a metal under normal test conditions is comparatively independent of specimen shape and size, and since with the available testing machines and methods it can be determined within satisfactory limits, the tensile strength may be used as a suitable criterion of the strain-hardening of a metal rather than the other mechanical properties. The slope of the curve showing the relation between the increase in tensile strength and the reduction in area by cold working

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[1] W. H. Bassett and C. H. Davis: Physical Characteristics of Commercial Copper-zinc Alloys. *Proc.* Inst. of Metals Div., A. I. M. E. (1928) 55.

may then be considered as the rate of strain-hardening. This gives a finite means for comparing the rate of strain-hardening of a given metal with that of any other cold-worked metal.

Upon cold-working a properly annealed wrought metal and making tests at various points throughout the range of working, we find that there is usually a constant increase in the tensile strength up to some transition point the location of which varies with the metal. Beyond this transition point there may be either a marked increase or decrease in the rate of strain-hardening of the metal. When there is a marked increase in the rate of strain-hardening the explanation appears to be that most of the available crystal slip planes have been utilized and there is a preferred orientation of grains throughout the material, with the result that further working tends to make the metal brittle but at the same time causes a marked increase in its tensile strength. If beyond the transition point there occurs a marked decrease in the rate of strain-hardening we usually find that the material has begun to fail by internal shear resulting not only in brittleness but also decrease in tensile strength.

The location of the transition point at which a marked change occurs in the rate of strain-hardening varies considerably with the different metals. For example, in aluminum and most of its wrought alloys cold working in excess of about 80 per cent. causes a marked increase in the rate of strain-hardening; for magnesium, failure by internal shear occurs after cold working about 45 per cent.; and in pure copper there appears to be no transition point. In any case, the relationship between the increase in tensile strength and the reduction in area by cold working may be expressed by the formula:

$$y = ax + ce^{dx}$$

wherein y = increase in tensile strength (in per cent.),

$\quad\quad x$ = the reduction in cross-sectional area (in per cent.),

a, c, and d are constants dependent upon the metal,

$\quad\quad$ and e = 2.71828 . . .

The first term of the right-hand part of this equation defines the relationship existing between the tensile strength and the cold working up to the transition point just referred to, while the second term in the same part of the equation is needed to define the relationship beyond the transition point. Most of the commercial cold-worked metal products are so fabricated that only part of the above equation is required to define the relationships existing between the tensile strengths and the cold working given to them; that is, the increase in tensile strength for amounts of cold working up to the transition point will be given by the simple equation

$$y = ax$$

wherein the terms have the same meaning as before. The constant a varies with different metals, as can be seen from the values given in Table 1.

TABLE 1.—*Values of the Constant a for Some Metals*

METAL	VALUE FOR a
Aluminum and all its commercial alloys	0.9
Copper	1.0
Brass, 72:28	1.8
High sheet brass, 66:34	1.8
Nickel silver, 71:11:18	1.15
Nickel silver, 55:27:18	1.15
Phosphor bronze, 95:5	1.8
Phosphor bronze, 92:8	1.8
Steel, low-carbon	1.7

The actual tensile strength of a cold-worked metal would then be given by the formula

$$T = To(1 + aR)$$

wherein T = the tensile strength in lb. per sq. in.,
To = the tensile strength of the properly annealed metal,
a = a constant dependent upon the metal,
R = the reduction in area expressed as a decimal.

When the relationship between cold working and the tensile strength of a metal has been defined, only the proper tensile strength values for the annealed metal are necessary in order to find the strengths of the various tempers resulting from given amounts of cold work. Approximate tensile strength values for different wrought metals in the properly annealed condition are indicated in Table 2.

TABLE 2.—*Approximate Values for the Tensile Strength of Some Annealed Wrought Metals*

METAL	TENSILE STRENGTH, LB. PER SQ. IN.
Aluminum (commercially pure)	14,000
Aluminum alloy (1.25 per cent. Mn)	15,500
Copper, pure	34,500
Brass, 72:28	45,000
High brass, 66:34	44,000
Nickel silver, 71:11:18	55,000
Nickel silver, 55:27:18	67,000
Phosphor bronze, 95:5	47,000
Phosphor bronze, 92:8	53,000
Steel, low-carbon	54,000

The values for brass, nickel silver and phosphor bronze in Table 2 were taken from Townsend, Straw and Davis,[2] those for steel, from the data reported by Comstock.[3]

The effect of cold working on the yield point of metals is somewhat more complex than on the tensile strength. This is due in part at least to the fact that metals which have been cold-worked do not have true yield points such as are found in tests of hot-rolled mild steel or wrought iron. What is termed "yield point" in the case of cold-worked metals then becomes largely a result of definition of the value. In this discussion "yield point" is defined as the stress causing a permanent set in the material of 0.2 per cent. Unfortunately, this arbitrary definition of yield point is not in general use, so test data are lacking for most of the metals. In the case of cold-worked aluminum, however, considerable test data are available and such data show that the effect of cold working on the yield point value is given by the following equation:

$$y = ax^b + ce^{dx}$$

wherein y = the increase in the yield point value (in per cent.),

x = amount of cold working (in per cent.),

a, b, c and d = constants dependent upon the material,

and e = 2.71828 . . .

As with the tensile strength equation, only part of the yield point equation need be used for the commercial intermediate tempers of aluminum. The actual yield point value then would be obtained from the formula

$$Y = Yo(1 + aR^b)$$

wherein Yo = yield point value of the annealed metal,

a = 3.34 (approximately),

R = the reduction in area expressed as a decimal,

and b = 0.36 (approximately).

This, however, is not a simple equation to use because of the exponent b. A much simpler way has been found to obtain the yield point value from the relationship existing between it and the tensile strength. This relationship is shown by the curve in Fig. 1, from which it may be noted that for annealed material the yield point is about one-third of the ultimate tensile strength. For 20 per cent. or more cold working the yield point is about 80 to 85 per cent. of the ultimate strength. Experience has shown that these approximate ratios will give sufficiently accurate yield point values when the tensile strength is known. From somewhat limited data available for other cold-worked metals it appears

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[2] J. R. Townsend, W. A. Straw and C. H. Davis: Physical Properties and Methods of Test for Some Sheet Non-Ferrous Metals. *Proc. Amer. Soc. Test. Mat.* (1929).

[3] G. F. Comstock: Wire Drawing and Properties of the Steel. *Iron Age* (1924) 621.

that the same relationship between yield point and ultimate tensile strength holds for these metals as in the case of aluminum.

From the fundamental equation just given it may be noted that the yield point value is appreciably affected by comparatively small amounts of cold working. For example, the ratio of yield point to tensile strength changes from a value of about 0.33 to 0.80 with only 20 per cent. cold working, starting with properly annealed metal. The yield point value therefore may be used as a rather sensitive index of the thoroughness of the annealing of a product.

The elongation value for a metal is affected to a considerable extent by the size and shape of the test specimen used as well as by the ductility of the material. Cold working decreases the ductility of a metal and therefore its elongation but on account of the effects of size and shape
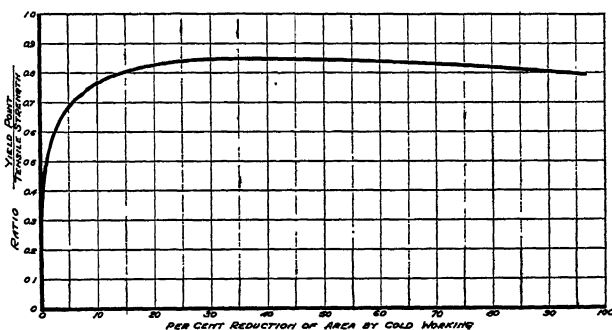
FIG. 1.—RELATIONSHIP BETWEEN YIELD POINT AND TENSILE STRENGTH.

of test specimens on the elongation value, the relationship between cold working and elongation varies appreciably. When round tensile test specimens having a constant value for the ratio of gage length to specimen diameter are used, however, the effects of specimen size and shape can be almost entirely eliminated from consideration. It is then possible to define quite accurately the relationship existing between cold work and the elongation occurring in a given gage length. The standard round tensile test specimen used in this country is ½ in. (or 0.505 in.) dia. with a 2-in. gage length, giving a value of 4D for the ratio of gage length in terms of the diameter of the specimen. As long as this ratio value is used, elongation values from round specimens about ⅛-in. dia., or larger, are directly comparable. For smaller specimens the errors involved in measurement of the elongation become too large for satisfactory results.

On the basis of using round tensile test specimens with gage lengths of four diameters, the decrease in elongation of wrought aluminum and its alloys resulting from cold working is expressed by the equation:

$$y = \frac{x}{a + bx}$$

wherein y = percentage decrease in the elongation in per cent.,

x = amount of cold working (reduction in area in per cent.),

a and b = constants.

The elongation value for any intermediate temper of wrought aluminum would then be given by the equation:

$$E = Eo\left(1 - \frac{R}{a + bR}\right)$$

wherein Eo = the elongation of the annealed product (using a round specimen and a gage length of 4 dia.),

R = reduction in area by cold working expressed as a decimal, ·

a = 0.20 (approximately),

b = 1.35 (approximately).

In testing the thin sheet and tubular products of metals, virtually a different size of test specimen is used for each thickness or size of product, so the equation just discussed will not give satisfactory values for elongation for these products. It may also be pointed out that the elongation value frequently varies considerably with the purity of the metal, the alloying constituents and the grain size of the product, the value of Eo being less definite for the different grades of aluminum than is, for example, the tensile strength. As in the case of the yield point, the elongation value changes rapidly during the initial cold working of an annealed product, but the elongation value is not always a satisfactory index of the degree of annealing, on account of the other factors just discussed and the errors of measurement involved in the test.

The equations just given, showing the relationship of cold working and elongation, are known to apply to aluminum (see Fig. 2) and there are many data in the published literature indicating quite definitely that these same equations are valid for other metals when the proper constants are used in them. ·

As there appears to be a rather definite relationship between the Brinell hardness of wrought metals and their tensile strength, we may assume with reasonable assurance that the Brinell hardness will be affected by cold working in a manner similar to the tensile strength, and experimental data appear to bear this out. The relationship between the Rockwell hardness of metals and cold working would in all probability be somewhat more complex, because of the relationship known to exist between Rockwell hardness and Brinell hardness.[4]

The Shore or scleroscope hardness of wrought metals appears to be dependent on their elastic limits, so we would expect the Shore hardness to vary about as the elastic limit varies with different amounts of cold working. The Shore hardness is also affected by numerous other factors

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[4] S. N. Petrenko: RelationsRolckwehips between the l and Brinell Numbers U. S. Bur. Stds. *Tech. Paper* 334.

such as thickness of specimen, surface condition of specimen and size of specimen support used in making the test. All of these facts result in giving a complex relationship between cold working and the Shore hardness values of a wrought metal and this relationship has not been satisfactorily defined.
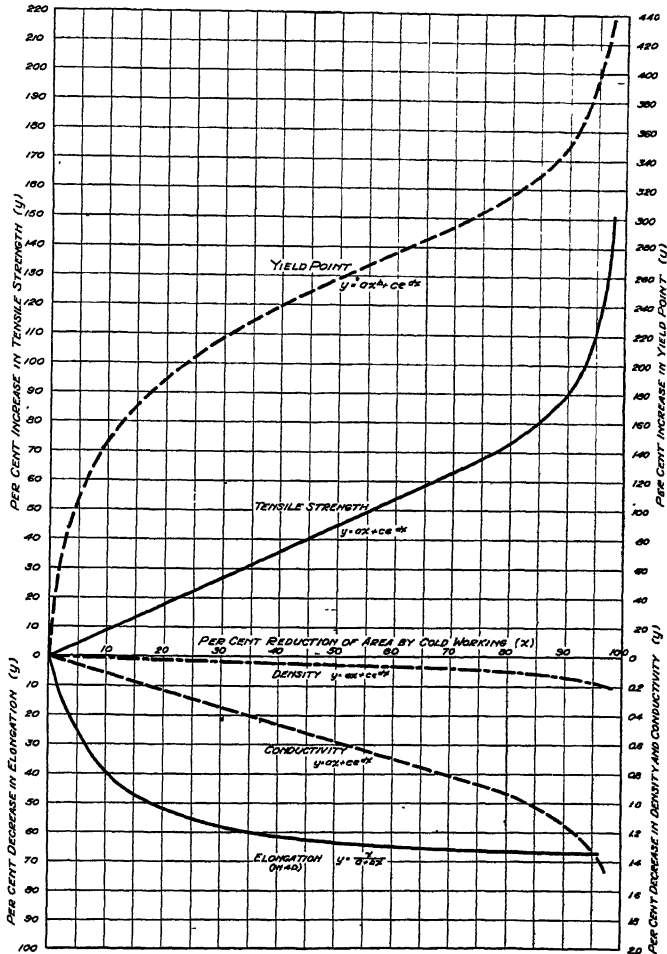
FIG. 2.—EFFECTS OF COLD WORKING UPON THE PHYSICAL PROPERTIES OF ALUMINUM.

There are two general procedures in common use for the production of various tempers of metal products: in many of the non-ferrous metals such as aluminum, brass and copper, various tempers are produced by putting definite amounts of cold working into the material after a final annealing, whereas in certain ferrous products it is customary to obtain intermediate tempers by partial annealing; that is, removing various

amounts of cold working after the product has been fabricated to the desired size. Experimental work with aluminum has indicated that the same combination of mechanical properties can be obtained irrespective of which procedure is followed. For practical reasons, however, it is customary to obtain these various tempers by cold working subsequent to a final annealing. With an understanding of the relationships between cold working and the physical properties of a metal it is possible to produce fabricated products of various forms from the given metal that will have quite similar properties irrespective of the form of product, the essential requirement being that the amount of cold working shall be the same in every case.

In certain metals, which can be hardened by heat treatment and then cold-worked, the same relationships between the amount of cold working and the physical properties have been found to obtain as when the same material is cold-worked after annealing. Outstanding examples of this are the aluminum alloys of the duralumin type, on which heat treatment may be followed by cold working so as to produce a material of high yield point, tensile strength and hardness but without much ductility. In applying the cold-working formulas for aluminum to such material we should use the mechanical property values of the normal heat-treated product as the basic ones instead of the annealed values.

Using a family of curves for a metal such as is shown in Fig. 2, it is possible to define a rational series of intermediate temper products to be made from the metal, and with a knowledge of the variations due to the fabrication processes involved, the variations in the physical properties of the products can be readily predicted.

DISCUSSION

G. F. COMSTOCK, Niagara Falls, N. Y. (written discussion).—There is only one question that I should like to ask Mr. Templin. About 10 years ago Alkins presented before the British Institute of Metals some data on copper somewhat similar to the results shown in Fig. 2 for aluminum, but he did not find that the tensile strength plotted against the reduction by cold working gave a smooth curve. About 5 years ago the writer showed, in *The Iron Age*, a set of similar curves for mild steel wire, and some of them gave marked indications of a break like that found by Alkins, while others did not. The author does not show the individual results from which his smooth curve in Fig. 2 was plotted, so we cannot judge whether or not there was any trace of a similar break in the curve for cold-worked aluminum. I should like to ask how the author's formula for the tensile strength of copper as related to the cold working would agree with the break in the curve found so distinctly by Alkins, and whether he would agree that such an irregularity does actually occur in progressive cold working?

R. L. TEMPLIN.—The work on copper to which Mr. Comstock referred is known to the writer. In that work a slight kink was found in the relationship curve near the center of the curve, that is, at about 50 per cent reduction in the cross-sectional area. That did not agree with some other published work on copper, and we found

that if we considered the curve to be a straight line, and simply neglected the kink, our results would check within something like less than 5 per cent, and that was considered close enough in view of the data presented.

Unfortunately it is not possible for us to give all the individual data that have been used to define the family of curves illustrated in the paper. There are over 200,000 tests available for defining the tensile strength curve below the transition point, and there are something like three times that number for defining the curve beyond the transition point. Those individual data could not have been put on that curve and have a diagram that would be presentable.

On the conductivity measurements, we have about the same number of tests for the right-hand portion of the curve, and quite a few less for the left-hand portion of the curve.

The tests that define elongation curves are on the order of dozens rather than tens of thousands, because they were made on round specimens having gage lengths of 4 dia. The tests on which we have data on the yield point run in the order of hundreds of determinations rather than tens or hundreds of thousands.

A. L. DAVIS, Waterbury, Conn.—On page 468, the third paragraph reads: "The character of the work done on metals appears to have comparatively little effect on the final mechanical properties obtained." The author speaks of its having been thoroughly run down in the instance of one or two metals, and infers that it will apply to all. I think there may be some doubt as to whether it does apply to *all* metals, under all circumstances.

The compressive yield point of common high brass is raised progressively by cold rolling. But if the reduction in thickness is effected by a direct squeeze—as between the face plates of a testing machine—the compressive yield point at every stage is higher than when the reduction is done by cold rolling, and after 40 per cent. reduction in thickness, the compressive yield point is 100,000 lb. per sq. in. as against 71,000 for cold rolling.

Another case showing that the character of work will affect the resulting hardness is the "Steckel" process of cold rolling thin metals, *while under heavy tension*. Repeated passages through the rolls, aggregating large percentages of reduction, are effected in that way, with a relatively small amount of hardening. Steel strips rolled in that way, receiving a total reduction of 90 per cent., will have a hardness about equivalent to what 40 per cent. reduction will give in the ordinary method of cold rolling, where there is no tension on the bar.

O. E. HARDER, Minneapolis, Minn.—Is it your opinion at the present time that fine-grain material and coarse-grain material show approximately the same yield point if they have approximately the same grain size?

R. L. TEMPLIN.—I do not think that is necessarily so. We depend more upon the ratio of yield point to the ultimate strength than on the ultimate alone as an index of the degree of annealing.

Regarding one of the points raised by Mr. Davis, we have made similar tests to those he indicated, whereby we squeezed a piece of metal in the testing machine for comparison with a rolled product, and we are always skeptical as to whether the surface conditions are truly representative of the conditions throughout the material, on account of the difference in surface friction conditions that obtain in working the metal under the two conditions indicated.

We are a little dubious about the use of Brinell hardness test for some of those explanations. We much prefer the tensile test. The hardening effect spoken of by one of the authors yesterday, measured by the Brinell hardness, can be gotten at rather readily by taking actual tensile tests from the different layers of the material, which we feel gives considerably more information.

P. D. MERICA, New York, N. Y.—Some time ago Mr. Webster, of the Bridgeport Brass Co., did some work on the study of the reduction of the area of metals, particularly copper, as effected by cold work, and he came to the conclusion that the reduction of area was an excellent criterion of the amount of cold work that had been carried out and somewhat better perhaps than the elongation.   Perhaps Mr. Templin would care to say something about any ideas he may have concerning the effect of cold work on reduction of area.

R. L. TEMPLIN.—Where the specimens used are of sufficient size, I can well agree that the reduction of area would probably be a good index in the case of many metals for studying the cold-working effects.   The elongation, as we usually measure it on sheet metals for instance, is not satisfactory.   That is due largely to the fact that we have virtually a different size of test piece for every thickness of metal, and with the tentative standard in this country of using a fixed gage length and a constant width of specimen, the elongation results are not a satisfactory criterion of the amount of cold working in the material.   The reduction of area, on the other hand, under certain conditions might well be a satisfactory index.

R. S. DEAN, Chicago, Ill.—I do not believe that tensile strength, or elongation, or reduction in area are entitled at all to be considered measures of cold work in the metal.   If we are going to define cold work by the reverse method, namely, by the properties produced by it, that is all right.   If we want to define it by the energy stored in the metal these properties are not a measure of it.   It is very simple to take a metal and produce exactly the same physical properties as far as we can measure them and yet have the metal in quite different states as regards energy content.

About two years ago, Mr. Zickrick and I showed[5] that copper could be given the same properties by cold working, and yet have very different annealing characteristics.   Now that difference in annealing characteristics indicates strongly that they have not the same amount of stored energy.

I would prefer to use something like the annealing characteristics, or, perhaps, temperature coefficient of hardness, something that measures either the total energy in the metal or the peak value of energy in the metal, as a measure of cold work.

I want to leave the thought that perhaps even all the mechanical properties may not vary with the tensile strength and reduction in area, but may be quite different, depending on past history.   The elastic after effect and fatigue limit may be such properties.

R. L. TEMPLIN.—We are primarily interested in determining the effects of cold working on the physical properties of the metals and consequently selected those properties which are determined most frequently, such as tensile strength, yield point and elongation.   We have also done a considerable amount of work on the fatique properties of aluminum and aluminum alloys.   This work shows that those properties are affected by cold working.

[5] R. S. Dean and L. Zickrick: Note on the Distribution of Energy in Worked Metals, etc.   *Proc.* Inst. of Metals Div., A. I. M. E. (1926) 207.

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Effect of Alloying on the Permissible Fiber Stress in Corrugated Zinc Roofing*

By E. A. Anderson,† Palmerton, Pa.

(Cleveland Meeting, September, 1929)

In another paper[1] the writer has shown that the low permissible maximum fiber stress in a loaded zinc sheet demands a much closer support spacing than is used for steel. The limiting fiber stress in 13-gage (0.032 in.) sheets having a 1-in. depth of corrugation was found to be about 5000 lb. per sq. in. on a 37-in. span under a load of 40 lb. per sq. ft. Corrugated steel sheets are commonly laid with spans varying from 48 to 60 in. In order to increase the span in 13-gage zinc to 54 in. (a common spacing) the metal must be capable of withstanding, under long-continued loading, a maximum fiber stress of about 10,000 lb. per sq. in. This is known to be impossible with unalloyed zinc.

In this paper the writer describes a series of experiments leading up to the development of an alloy capable of safely sustaining this fiber stress. The effect of alloying on the slow creep of zinc was studied by means of static tensile tests, accurate determinations of apparent elastic limits and finally by means of loading tests on full-size roof sections. Two industrial buildings roofed with alloyed zinc sheets on spans involving fiber stresses in excess of 10,000 lb. per sq. in. have been under observation for over two years without signs of sagging.

EXPERIMENTAL WORK

Two methods of increasing. the maximum permissible fiber stress in zinc were considered. Cold rolling, which increases the stiffness and tensile strength, was found to decrease the resistance to slow flow. Alloying, therefore, provided the only feasible means of obtaining the desired result.

It was recognized that the improvement secured by the solid solution of natural impurities was insufficient. A series of alloys was outlined, therefore, in which a number of metals were added separately and together. The sheets rolled from these alloys were tested under

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static tensile loads to study the effects of the various added elements on the slow creep of zinc.   Certain of the results of the preliminary tests are compiled in Table 1.

TABLE 1.—*Static Tensile Tests on Preliminary Alloys*
Prime Western Zinc Base

Mark	Composition	Tensile Strength, Lb. per Sq. In.	Time to 10 Per Cent. Elong. under Load of 12,000 Lb. per Sq. In. Minutes
1	2.4 Cu	36,700	204
2	0.01 Mg		2,820
3	No additions	28,000	330

Magnesium, which does not go into solid solution in zinc but rather forms a hard brittle compound, had the most advantageous effect.   In order to determine the possible added advantage of an element that would go into solid solution in zinc, 1 per cent. of copper was added, which is below the limit of solid solubility of copper in zinc.   The results of static tensile tests on four alloys are given in Table 2.

TABLE 2.—*Static Tensile Tests on Alloys Containing Copper and/ or Magnesium*
Prime Western Zinc Base

Mark	Composition	Tensile Strength, Lb. per Sq. In.	Time to 10 Per Cent. Elong under Load of 10,000 Lb. per Sq. In., Minutes
C	Unalloyed	25,100	420
K	1.0 Cu	34,600	11,200
L	0.01 Mg	40,200	17,200
D	1.0 Cu + 0.01 Mg	43,800	216,000

The improved resistance to slow flow achieved by the addition of copper and magnesium to zinc is outstanding.   The alloy designated as "D" was selected for further study.

Apparent Elastic Limit

The writer has previously presented data indicating a close agreement between the apparent elastic limit in zinc and the maximum permissible fiber stress.   Prof. H. F. Moore, in his laboratories at the University of

Illinois, made a number of determinations by the J. B. Johnson method.[2] The results will be found in Table 3.

TABLE 3.—*Johnson Apparent Elastic Limits of Commercial Rolled (Prime Western) Zinc and Alloy D*

Mark[a]	Rate of Stretch, Inches per Minute		Unit Stress, Lb. per Sq. In.		Elong. in 2 In. Per Cent.	Temperature, Deg. C.
	Below Johnson Limit	At Ultimate Load	At Johnson Limit	At Rupture		
C-W	0.000243	0.034	5,200	18,200	49	23.5
C-W	0.00107	0.65	5,800	21,200	43	23.0
C-W	0.0026	0.097	6,000	19,500	33	23.0
C-A	0.000207	0.039	10,300	28,200	20	24 0
C-A	0.00095	0.75	10,500	29,500	14	23.0
C-A	0.00253	0.113	12,500	28,300	19	23.0
D-W	0.00020	0.0403	13,500	34,100	21	21.0
D-W	0.00085	0.272	15,200	37,800	13	25.5
D-W	0.0019	0.100	14,800	33,800	17	26.0
D-A	0.00022	0.033	20,100	42,300	4	23.0
D-A	0.00081	0.025	22,750	42,700	4	25.5
D-A	0.0022	0.025	22,200	42,500	3	26.0

[a] W = with grain; A = across grain; C = Prime Western zinc, commercial rolled.

It was evident, from these data, that if the same relationship holds between the apparent elastic limit and the maximum permissible fiber stress that was noted for unalloyed zinc, the sheet steel purlin spacing at which we aimed could be attained with this alloy.

Sheet Loading Tests

To confirm this relation, loading tests on full-size roof sections were made to determine the maximum permissible span under a uniform load of 40 lb. per sq ft. The method of conducting such tests has been previously described.[3] From the permissible span data the maximum fiber stress was calculated for the various safe conditions. The data will be found in Table 4, together with previously determined information on unalloyed zinc.

The spans used are those that permit a deflection of less than 0.75 per cent. of the span when loaded to 40 lb. per sq. ft. for 20 days. This test has been found by the writer[4] to be a reliable means of determining safe load for service conditions. A greater deflection under the same

[2] A. S. T. M. Tentative Standards (1927) 1075, Method 2.

[3] W. M. Pierce and E. A. Anderson: *Op. cit.*

[4] W. M. Peirce and E. A. Anderson: *Op. cit.*

test conditions will result in rapid, continuous sagging if the loading is continued. Where lighter loads can be assumed, longer spans are theoretically possible without exceeding the safe maximum stress. Practically, on longer spans, the sheets lack the necessary rigidity to meet temporary loads, such as men walking on the roof, without undue elastic deflection.

TABLE 4.—*Permissible Spans and Fiber Stresses in Corrugated Alloy D and Unalloyed Zinc Sheets under a Load of 40 Pounds per Square Foot*

Mark	Gage, Inches	Depth of Corrugation, Inches	Permissible Span, Inches	Maximum Fiber Stress, Lb. per Sq. In.
C	0.032	7/8	34.5	5,215
D	0.032	7/8	48.0	9,639
C	0.032	1	37.0	5,110
D	0.032	1	54.0	10,125
C	0.036	1	39.5	4,722
D	0.036	1	57.0	9,983
C	0.040	1	41.0	4,397
D	0.040	1	60.0	9,865
C	0.045	1	42.5	4,136
D	0.045	1	64.0	9,705

Average fiber stress, unalloyed zinc (C) = 4,700 lb. per sq. in.
Average fiber stress, D   = 9,863 lb. per sq. in.

Comparing the safe working stresses determined by actual static loading with the Johnson apparent elastic limit, which is determined by relatively rapid loading, we find that the agreement, while close enough to serve as a useful check, is not as close as the writer found in the case of commercial rolled zinc. In other words, the effect of increasing the rate of loading on the apparent elastic limit is greater in the case of the alloy.

Static Tensile Tests

Static tensile tests were made on the alloy D at 20°, 40° and 60° C. at loads of 5000, 8000, 12,000, and 18,000 lb. per sq. in. in comparison with soft rolled Brass Special zinc, which has the highest resistance to slow flow of the unalloyed zincs tested. The log rate of flow has been plotted against load in Fig. 1.

The data given in Fig. 1 were obtained on samples of D which were not rolled under as favorable conditions as were later developed. It will be noted, however, that at the recommended fiber stress (10,000 lb. per sq. in.) the alloy shows a marked superiority in resistance to flow over unalloyed zinc. At 60° C. and with much lighter loads the two metals have virtually identical characteristics. This combination of load and temperature is never realized, however, in the use of corrugated roofing, hence this condition is of no engineering importance.

In unalloyed zinc it was noted that cold rolling increased the tensile strength but decreased the resistance to slow flow. The same condition was found in the alloy. Tensile strengths as high as 60,000 lb. per sq. in. are possible, but the resistance of such material to creep is greatly inferior to that of the same alloy rolled to a tensile strength of only 35,000 pounds per square inch.
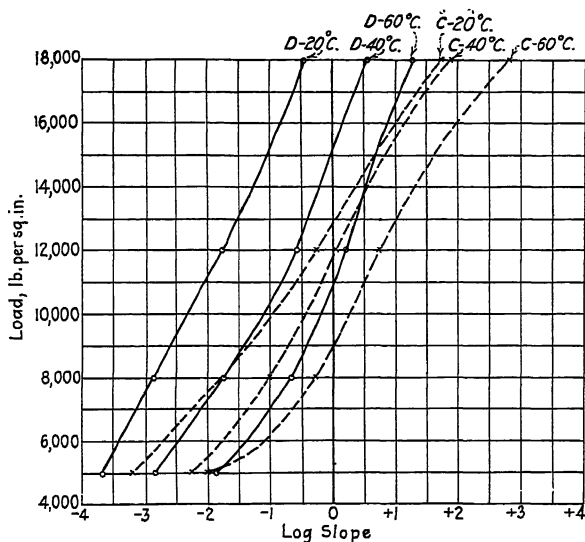
FIG. 1.—LOG SLOPE-LOAD CURVES FOR UNALLOYED ZINC AND ALLOY D.

Metallography

While the details of the constitution of the zinc corner of the Zn-Cu-Mg system are not entirely clear, certain interesting facts have been disclosed. Copper in the amount added to D goes into solid solution in zinc. Magnesium, on the other hand, forms the compound $MgZn_2$, which in turn forms a eutectic with zinc containing only 4 per cent. of the compound. Thus 0.1 per cent. of magnesium will form 2.5 per cent. of eutectic.

As would be expected from the equilibrium relations known to exist in the binary alloys, copper added to zinc causes a change in lattice dimensions as determined by X-ray methods, while magnesium does not. When magnesium is added to zinc containing copper in solid solution, however, a change in lattice dimensions results which is probably associated with the increased resistance to plastic flow.

The recrystallization temperature of zinc is raised by the alloying constituents from room temperature to approximately 200° C. It is possible to work and anneal the metal in much the same way as is done with brass.

Toughness

A metal roofing of commercial value must be capable of being erected in freezing weather without danger of cracking when riveted and must resist the impact of falling objects such as icicles. To investigate the value of alloy D in this connection corrugated sheets of the alloy and of
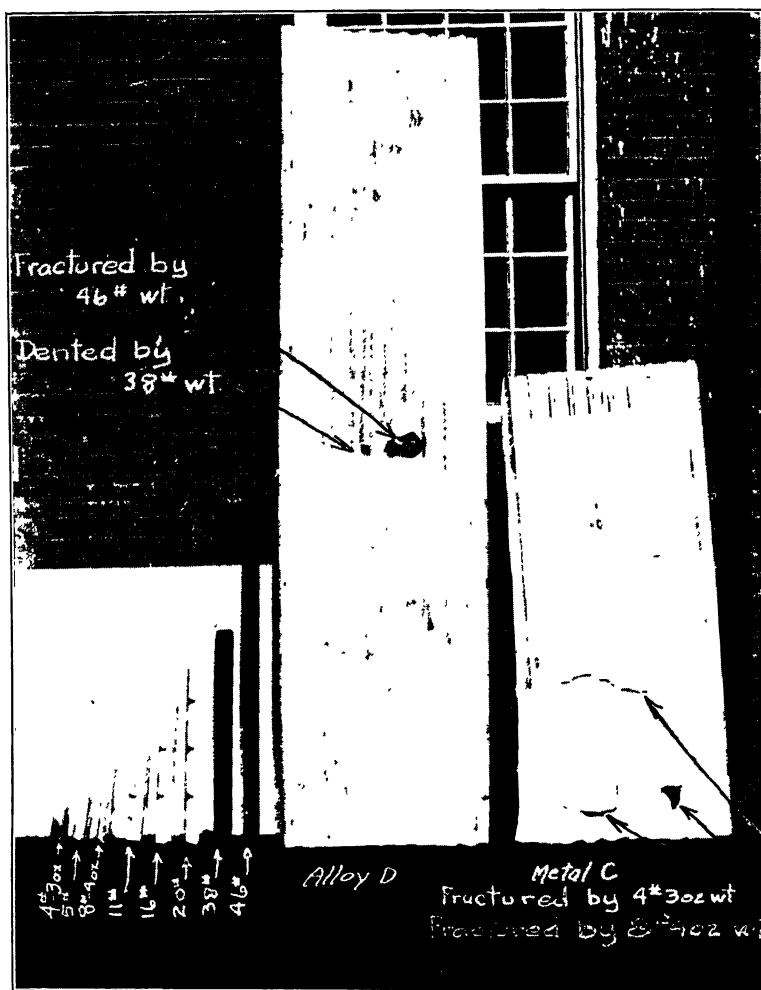
FIG. 2.—LOW-TEMPERATURE IMPACT RESISTANCE OF UNALLOYED ZINC AND ALLOY D.

unalloyed zinc were placed on supports and subjected to shock stresses by dropping various weights on the center of the span from a height of 12 ft. Under these conditions, and at a temperature of 30° F., a 4½-lb. bar split the unalloyed sheet from side to side; a 38-lb. bar failed to tear the alloy sheet; a 46-lb. bar punched a smooth round hole through the

sheet but did not crack it. The low-temperature toughness imparted by alloying is clearly evident in Fig. 2.

Summary

An alloy of zinc containing 1 per cent. of copper and 0.01 per cent. of magnesium has been studied.

The tensile strength of the rolled alloy as compared with the tensile strength of the rolled unalloyed base is 35,000 to 60,000 lb. per sq. in. as against 20,000 to 30,000 lb. per sq. in. The alloy is also much tougher at freezing temperatures.

The apparent elastic limit determined by the Johnson method is above 13,500 lb. per sq. in. with the grain as compared with 5200 lb. per sq. in. for the unalloyed base.

Loading tests on roof sections confirmed by roof installations show that the higher apparent elastic limit makes it possible to utilize these sheets for roofing on much greater purlin spacings than those safe for ordinary zinc; reaching, in fact, a large range of the spacings used for steel sheets.

DISCUSSION

G. F. Comstock, Niagara Falls, N. Y. (written discussion).—A good roofing material obviously should have not only sufficient mechanical strength but also good resistance to corrosion. The data presented in this paper show in an interesting way how the strength of zinc sheets may be improved by alloying, but nothing is said as to how this alloying may affect the corrosion resistance.

Some experiments carried out by the writer a few years ago indicated that the presence of copper in zinc reduced its resistance to corrosion, and it would not be at all surprising if the presence of magnesium might be found to have a still greater effect in the same direction.

Some information as to the corrosion resistance of the alloyed zinc sheet would certainly add greatly to the value of this paper. If the lasting quality of this roofing material should turn out to be no greater than that of good zinc-coated iron, the fact that its strength is equal to that of the sheet iron would be of small practical significance.

E. A. Anderson.—We have made a great many corrosion tests, but we did not include any of them in the paper. Possibly Mr. Comstock used a different grade of zinc. The composition of the zinc alters the corrosion properties greatly. It is entirely a question of film formation, protective films forming with certain impurities present in the zinc. The copper seems to act to build a more tenacious film, and the

atmospheric weathering resistance of the alloy as prepared commercially is about 30 per cent. better than that of unalloyed zinc.

E. M. WISE, Bayonne, N. J.—In view of the rather spectacular effect produced by such a small quantity of magnesium, the question arises as to whether the magnesium was present as a compound, or perhaps as an oxide. Have any determinations been made of relative grain sizes after a given rolling schedule, or thermal treatment, which would be indicative of any grain growth retarding the effect of oxide, if present? Perhaps a compound will do the same thing, but the solubility of the compound must be extraordinarily low for it to be present in a free state.

E. A. ANDERSON.—The magnesium is insoluble in zinc. Whether it is soluble in the presence of copper, and to what extent, we do not know. It is difficult to see in the microstructure. We suspect that there is some solubility in the presence of copper, but it is not evident.

We have never investigated to see whether the magnesium is present as oxide or not. The spectroscope was used for the analytical work, as the amount of magnesium is so small that it is hardly detectable chemically. The spectroscope tells us that there is virtually the amount there that we added—as to the form, we do not know.

The material handles very much like a brass. Ordinarily zinc can be hot-rolled and recrystallized at room temperature, and cannot be annealed without ruining the properties, the grain growth is so rapid—too rapid to render annealing a commercial proposition. The alloy, however, can be cold-rolled and annealed exactly as a brass can be. It is virtually a brass with only 1 per cent. copper. Copper distorts the space lattice of zinc. Magnesium alone produces no measurable effect. Magnesium added to a zinc-copper alloy produces a further distortion of the zinc lattice. The mechanism of the hardening is possibly tied up with this distortion of the space lattice although we are not certain exactly how that ties in.

E. M. WISE.—There is no evidence of precipitation hardening?

E. A. ANDERSON.—No, we have tried to find it. Every once in a while we have been afraid that we had missed it, and have tried again. Annealing at high temperature followed by reannealing at lower temperatures produces no change that we can measure in any of the properties. It seems to be simply a space distortion affair, and the mechanism is not clear.

W. B. PRICE, Waterbury, Conn.—I was going to ask practically the same question of Mr. Anderson—whether there was any possibility of a very small amount of silicon being introduced, and any dispersion hardness taking place through magnesium silicide? Has that been investigated?

E. A. ANDERSON.—The silicon has not been investigated in this particular alloy. Zinc and silicon are not very friendly, and we have never been able to get them to match up together and do anything important. Careful analyses of zinc over a period of several years failed to show any silicon present, even when melted in a silicon crucible, or when we have deliberately added silicon. It is possible that the magnesium might bring some silicon into the alloy, although I think that is somewhat questionable because the alloy can be prepared in the pure graphite crucible, that is, one without clay, and still have its exceptional properties.

It seems to be independent of the purity of the alloying additions and the sort of crucible used. I cannot believe, on the basis of our present experience, that any little variations have been creeping in that might alter the situation, because it remains remarkably constant regardless of what we do. I am still inclined to think that the alteration of the X-ray structure is the best explanation.

R. F. Mehl, Anacostia, D. C.—With respect to the true elastic limit of zinc: I believe Mr. Anderson remarked that there appears to be none. Actual measurements on zinc crystals by Schmidt and his coworkers in Germany have shown that there is a critical shear of 36 g. per sq. mm. on the plane of slip, below which no slip of any type takes place and above which there does. This is considerably below the ordinary yield point, but it does seem to be a fundamental elastic limit.

E. A. Anderson.—I do not know offhand how the grams and millimeters calculate out, in terms of pounds per square inch, but we have tested zinc specimens having a tensile strength of 20,000 lb. per sq. in., under a load as low as 2500, and have broken them by letting them slowly creep over a period of 2½ years. So far we have found no loading test where a load has been suspended from a specimen that has been so low that we could not stretch or break the specimen. It calculates out that a 1000-lb. load will break in 65 years. We may report on that.

Effect of Heat Treatment on Properties and Microstructure of Britannia Metal

By B. Egeberg* and H. B. Smith,* Meriden, Conn.

In a previous paper[1] the authors dealt with the physical properties of cold-rolled and heat-treated Britannia metal of the approximate composition Sn, 91 per cent., Sb, 7 per cent. and Cu, 2 per cent. It was found that cold rolling to more than 50 per cent. reduction produced a continuous softening of the metal when measured by the Brinell machine, whereas the Shore instrument indicated increased hardness; that the strength of the material followed the Brinell hardness and that the metal therefore became weaker the more it was cold-rolled; and further, it was found that hardness and strength could be largely restored to the cold-rolled metal by "baking" for about one hour at any temperature between 200° and 450° F., the melting point. The higher the baking temperature, the more effective was the heat treatment as far as increased hardness was concerned.

It seemed to be of little importance whether the metal was soaked or not at the baking temperature for a great length of time and the rate of cooling seemed to be immaterial.

The present paper deals with the same alloy and more particularly with the resistance towards various forms of stress — tensile, bend and deep drawing. The metallography of Britannia metal has in part also been covered and an explanation attempted for the abnormal behavior of this alloy.

Tensile and Bend Tests

Two ingots 7¾ in. wide, 11 in. long and ¾ in. thick were cast from the same pot. One ingot was cold-rolled in one direction to a strip 0.241 in. thick, which furnished the tensile test specimens; the other ingot was rolled in the same way to 0.253 in. and furnished the specimens for the bend tests. The ingots were cast as described in the previous paper and cold-rolled in six passes.

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[1] B. Egeberg and H. B. Smith: Effect of Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal. *Trans.* A. I. M. E., Inst. Metals Div. (1929) 373.

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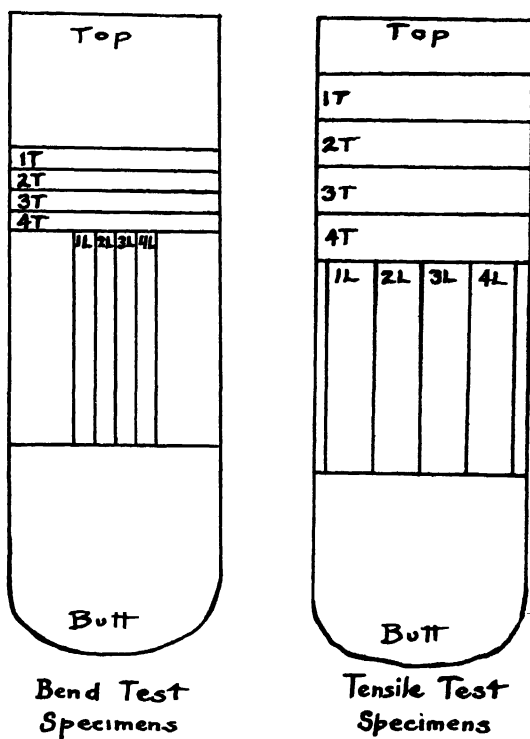
FIG. 1.—SECTIONS OF INGOTS SHOWING LOCATION OF TEST SPECIMENS.
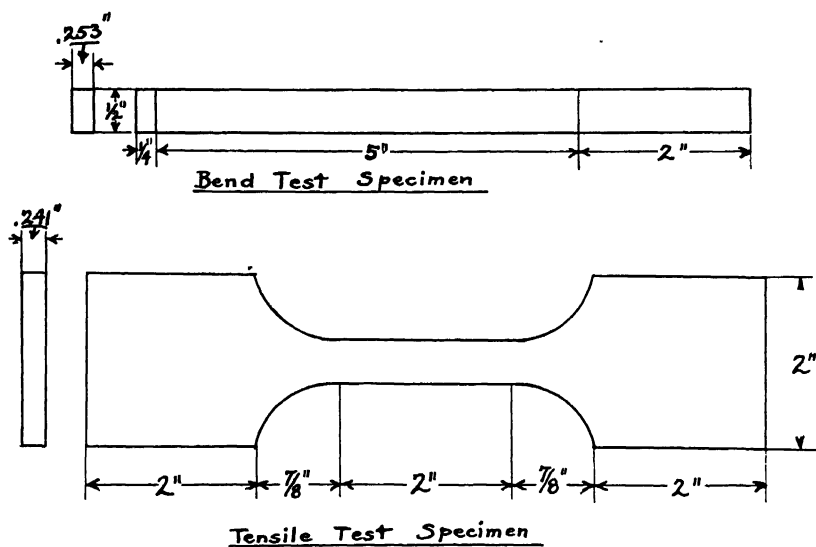
FIG. 2.—DIMENSIONS OF TEST SPECIMENS.

The specimens, both longitudinal and transverse, were all cut from the section of the strips that correspond to the middle part of the ingot, the location being shown on Fig. 1. The dimensions of the tensile and bend test specimens are given in Fig. 2. None of the samples was machined on the rolled surface, which was smooth and bright. The treatment and Brinell hardness of the specimens are shown in Table 1. The baking was done at 400° F. in a furnace controlled by pyrometer as described in detail in the previous paper. The samples were in the furnace for 1 hr. then were air-cooled. The Brinell hardness figures refer to 100-kg. load, 10-mm. ball dia. applied for 30 seconds.

TABLE 1.—*Brinell Hardness of Britannia Metal Specimens*

Treatment	Tensile Test Specimens		Bend Test Specimens	
	Number of Sample	Brinell Hardness	Number of Sample	Brinell Hardness
Cold-rolled..	2L	8 04	4L	8.04
Cold-rolled and baked ..	1L	9.49	1L	9.49
Cold-rolled...... .. .	4T	7.43	2T	8.04
Cold-rolled and baked.... .	1T	9.49	1T	9.49

TABLE 2.—*Results of Tensile Tests*

Treatment	Number of Sample	Maximum Tensile Strength, Lb. per Sq. In.	Breaking Load, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
Cold-rolled..	2L	7550	3410	50
Cold-rolled and baked...	1L	8620	4550	40
Cold-rolled.............	4T	8470	4660	35
Cold-rolled and baked.......... .	1T	8830	6480	29

The results of the tensile tests are collected in Table 2. Baking produces some increase in the maximum tensile strength and considerable increase in the breaking load. The elongation is correspondingly reduced. It should also be noted that the metal is strongest in the transverse direction. It was not possible to discern any elastic or proportional limit during the test. It was shown in the previous paper that the increased strength obtained by baking is minimized by the following cold work. Such great deformation took place during the pulling test, before the maximum tensile strength was reached, that no great difference in tensile strength was expected between cold-rolled and baked samples.

It was thought that baking would have considerable influence upon the elastic limit, therefore bend tests were undertaken in the way illustrated by Fig. 3, in the hope that this method of testing would throw more light upon the elasticity of the alloy than was obtained by the tensile test.

The samples were clamped on one end between flat jaws, which held them in a horizontal position. The other end was loaded and unloaded by increasing weights and the deflections were measured by the transit. The results are given in Table 3. The samples that were cold-rolled only, both longitudinal and transverse, started to flow at a load of 3500 g. on the scale pan, whereas the baked samples showed the same characteristic only after a load of 5000 g. Further, the unbaked samples gave an elastic limit of 1500 to 2000 g. load against 3500 g. for the baked samples. Up to that point no deflection was observed after unloading; over this point they take a permanent set, which increases with increasing loads up to the flow point. After the flow point is reached, the longer the load is left on the more the samples bend, making definite readings impossible.
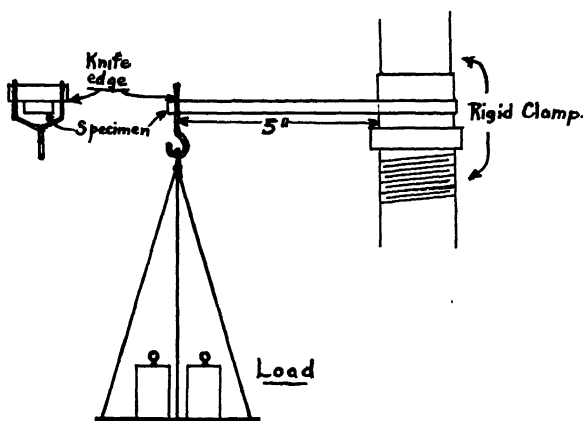
FIG. 3.—APPARATUS FOR MAKING BEND TESTS.

Applying the formula $W = \dfrac{f \times s}{l}$ for a beam under bending, the elastic limit for the cold-rolled specimens 4L and 2T were calculated respectively to 3087 and 4116 lb. per sq. in., whereas the baked specimens 1L and 1T both gave an elastic limit of 7204 lb. per sq. in.

As mentioned, the samples were rolled from an ingot $\frac{3}{4}$ in. thick to a strip 0.253 in. thick. The previous paper showed that if the sample were rolled to a commercial size, for example, 0.036 in., further reduction of the strength would have been produced during cold rolling and a correspondingly larger increase would have been obtained during the baking process. The actual difference in elastic strength between cold-rolled and heat-treated Britannia metal depends, therefore, not only on the baking temperature but also on the previous mechanical treatment. Dealing with commercial conditions, it can be said that deformation of baked articles requires the application of at least twice the force needed for those not baked.

TABLE 3.—*Bend Tests on Britannia Metal*

Load, Grams	Cold-rolled		Cold-rolled and Baked at 400° F. for 1 Hr.	
	Sample 4L Deflection	Sample 2T Deflection	Sample 1L Deflection	Sample 1T Deflection
500	1	1	0	0
0	0	0	0	0
1000	1	1	1	0
0	0	0	0	0
1500	4 elastic limit	1	1	1
0	2	0	0	0
2000	5	4 elastic limit	1	1
0	2	2	0	0
2500	6	6	1	1
0	4	4	0	0
3000	9	9	2	3
0	6	7	1	0
3500	Continuous flow during load		3	3
0			1 elastic limit	1 elastic limit
4000	Continuous flow during load		6	5
0			3	3
4500	Continuous flow during load		10	8
0			7	5
5000	Continuous flow during load		Continuous flow during load	

In order to test the permanency of the effect produced by baking, four bend test samples, of which two had been baked and two were as cold-rolled, were aged for 6 months at room temperature. The hardness before and after aging is given in Table 4. For location from which the test specimens were cut, see Fig. 1. There was a slight increase in hardness after aging in both the cold-rolled and baked samples.

The bend tests, carried out as described, gave the results set down in Table 5. Comparison of this table with Table 3 shows that neither the cold-rolled nor the baked material was changed noticeably in strength by aging over a period of 6 months.

TABLE 4.—*Effect of Aging on Hardness of Cold-rolled and Baked Britannia Metal*

Number of Sample	Treatment	Brinell Hardness	
		After Rolling	After Aging
2L	Cold-rolled................ ...	8 49	8.49
3L	Cold-rolled and baked	9.49	10.1
4T	Cold-rolled..	8.04	8.49
3T	Cold-rolled and baked.....	9.49	10.1

TABLE 5.—*Bend Tests on Britannia Metal Aged for Six Months at Room Temperature*

Load, Grams	Cold-rolled and Aged		Cold-rolled, Baked at 400° F. for 1 Hr. and Aged	
	Sample 2L Deflection	Sample 4T Deflection	Sample 3L Deflection	Sample 3T Deflection
500	1	1	1	1
0	0	0	0	0
1000	3	2	1	1
0	1	0	0	0
1500	5 elastic limit	3	2	2
0	2	0	0	0
2000	7	5 elastic limit	3	3
0	4	2	0	0
2500	10	9	4	3
0	8	7	0	0
3000	14	14	4	4
0	12	11	1	0
3500	Continuous flow during load		6	6
0			2 elastic limit	2 elastic limit
4000	Continuous flow during load		9	9
0			4	5
4500	Continuous flow during load		15	14
0			11	11
5000	Continuous flow during load		Continuous flow during load	
0				

Calculation according to formula $W = \dfrac{f \times s}{l}$ gave elastic limits 3087 and 4117 lb. per sq. in. for the cold-rolled and aged samples and 7204 lb. per sq. in. for the baked and aged samples, which are identical with the results obtained before aging.

DUCTILITY

Samples from a sheet 0.051 in. thick, both as cold-rolled and as baked for 1 hr. at 400° F. and air-cooled, were tested with a standard Erichsen tester. The results were: as rolled, 11.7 and 11.6 mm.; as baked, 9.7 and 9.6 mm. These figures correspond with the tensile test data in Table 2; namely, that baking reduces the ductility.

MICROSTRUCTURE AND HARDNESS

A cast plate 7¾ by 11 in. and 0.730 in. thick was rolled and sampled according to Table 6. Brinell hardness determinations were made on the various reductions both in the cold-rolled and in the baked condition. Brinell figures, as before, refer to a 10-mm. dia. ball, 100-kg. load applied

TABLE 6.—*Brinell Hardness after Various Cold Reductions before and after Baking*

Thickness, Inches	Reduction, Per Cent.	Brinell Hardness		Microstructure Shown in	
		As Rolled	After Baking 90 Min. at 400° F. Air-cooled		
0.730	0	11.0	10.4	As cast Fig. 4 Fig. 5	Baked Fig. 6
0.569	22 0	12.5	10.1	As rolled Fig. 7	Fig. 8
0.439	39.8	11.4	9.77	Fig. 9	Fig. 10
0 303	58.5	9.77	9.77	Fig. 11	Fig. 12
0.157	79.4	8.26	9 49	Fig. 13	Fig. 14
0.076	92.4	7.06	9.49	Fig. 15	Fig. 16
0.045	95.5	5 81	8.97	Fig. 17	Fig. 18

for 30 sec. Photomicrographs were obtained on the cast metal and on various reductions down to a sheet 0.045 in. thick.

The sections prepared for the microscope were all cross-sections with the exception of Fig. 4, which represents the etched surface of
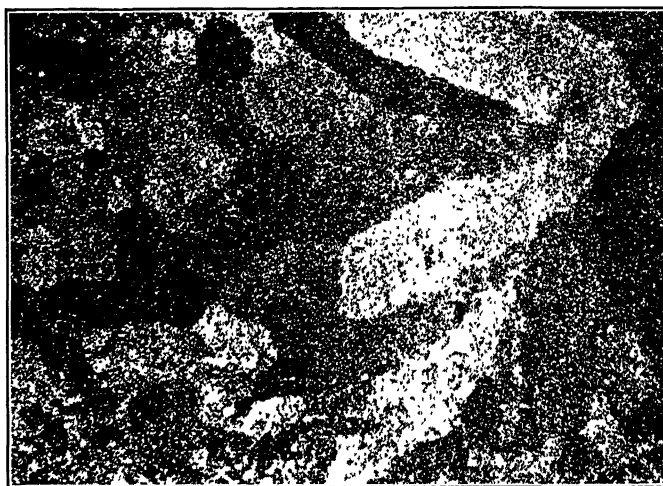
FIG. 4.—ETCHED SURFACE OF CAST PLATE NEAR GATE. × 2.

the cast plate near the gate, where the grains were exceptionally large. The sections were cut with a hack saw, filed and ground on emery paper, moistened with a solution of paraffin wax in kerosene, and the distorted surface was removed by strong nitric acid; they were polished on a broad cloth wheel with levigated alumina used with a thick soap solution.

The samples were etched with a solution consisting of 1 part concentrated nitric acid, 3 parts acetic acid and 15 parts glycerin, the surface was again lightly polished and again etched, this process being repeated until the correct structure appeared. This method of preparing the microsections is substantially the same as that described by Vilella and Beregekoff,[2] except that we have found that the use of strong nitric acid facilitates the operation and materially decreases the amount of manual labor involved, as it does away with all hand rubbing.

The grain in the cast condition can be seen readily with the naked eye (Fig. 4). This grain persists in the cold-rolled samples and can be seen vaguely by the naked eye—though impossible to discern with the micro-
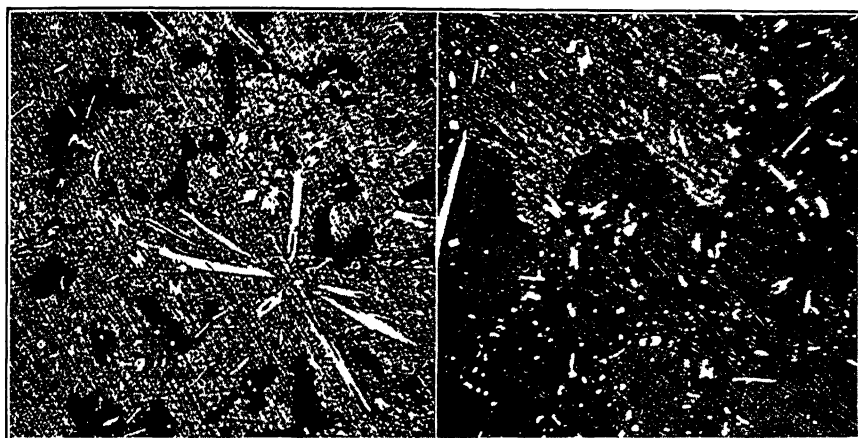
FIG. 5.—CROSS-SECTION AS CAST. × 250.   FIG. 6.—CAST AND BAKED. × 250.

scope—on the etched surface down to about 40 per cent. reduction, when it seems to disappear. In samples reduced more than 40 per cent., no grains can be discerned either by the naked eye or by the microscope.

The grains evidently flow progressively into one another with increased reductions. In order to understand such a happening, it should be noted that when two specimens were polished and etched together in one clamp, it happened occasionally that grains from one of the specimens were partly carried over the boundary line into the other specimen, leaving part of the grain on each side of this line. Such squeezing into one another of the grains during cold rolling would explain why the grains on the etched surface are visible to the naked eye after slight cold reduction, whereas we were unable to locate the grain boundaries when using the microscope. It would also explain why by further reduction the grains become invisible to

[2] J. R. Vilella and D. Beregekoff: Polishing and Etching Lead, Tin and Some of Their Alloys for Microscopic Examination. *Ind. & Eng. Chem.* (1927) **19.**
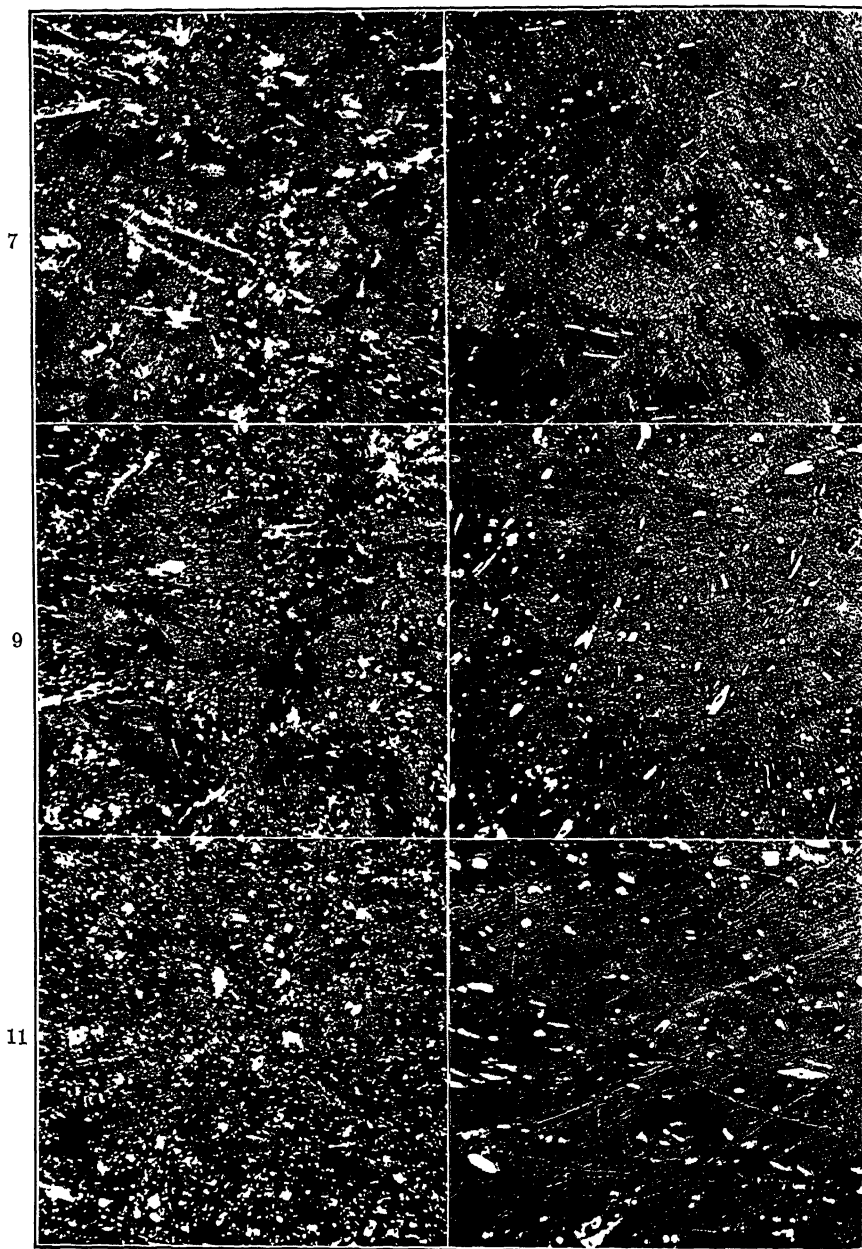
FIG.   7.—AS ROLLED.   SIZE 0.569 IN.; 22 PER CENT. REDUCTION.
FIG.   8.—SAME AS FIG. 7, BAKED.
FIG.   9.—AS ROLLED.   SIZE 0.439 IN.; 39.8 PER CENT. REDUCTION.
FIG. 10.—SAME AS FIG. 9, BAKED.
FIG. 11.—AS ROLLED.   SIZE 0.303 IN.; 58.5 PER CENT. REDUCTION.
FIG. 12.—SAME AS FIG. 11, BAKED.
ALL FIGURES, × 250.

the naked eye though originally of such size that this should be feasible (see Fig. 4). This would lead to the conclusion that Britannia metal, and probably similar tin-base alloys, when sufficiently cold-rolled is not a crystalline aggregate in the common sense, but consists of one mass in which the original crystals do not exist as such but have lost their individuality at least as far as their boundaries are concerned.

The baked samples all show a recrystallized grain and grain boundaries can be developed easily in samples from all reductions. The photomicrographs from these samples (Figs. 8, 10, 12, 14, 16 and 18) show less white constituent than in the corresponding samples before baking (Figs. 7, 9, 11, 13, 15 and 17). It is reasonable, therefore, to assume that the increased strength and hardness brought about by baking is due to the white constituent largely being brought into solid solution, as indicated in the previous paper.

Conversely, the weakening of the samples reduced more than 40 to 50 per cent. in cold rolling might be due partly to the precipitation of white constituent, as evidently the cast specimen, to judge from the photomicrography, does not contain as much of this constituent as the cold-rolled samples show. Furthermore, additional loss in hardness and strength by continued cold rolling is caused by the breaking up of the harder and stiffer white constituent in the form of needles and coarse particles of considerable interlacing strength into small particles which offer little resistance to deformation (compare Figs. 5 and 7 with Fig. 13, for example).

At reductions lower than 40 per cent. Britannia metal behaves in the normal manner (see Table 6), in that it becomes harder when cold-rolled and is softened by application of heat, which is just opposite to its behavior at greater reduction (see discussion by O. W. Ellis of the previous paper). Evidently the hardness of any sample depends on several factors, the influence of which change in relative magnitude with the reductions given. In cold-rolled metal, there is apparently a tendency towards increased hardness, as is normal for any metal after cold deformation, and at the same time there is a decrease in resistance towards deformation by the Brinell ball due to precipitation of some white constituent from solid solution and to the breaking up of the interlaced structure of the white constituent already on hand, which two latter effects become more pronounced with increased reductions. The former effect, on the other hand, is prevented from attaining any considerable magnitude, by the heat generated by the cold deformation. In commercial rolling, which is considered here, the metal becomes heated to such an extent that it is hardly possible to handle it with bare hands. It is not surprising that this heat is effective in minimizing strains, considering the great plasticity of the metal at temperatures far below its melting point (450° F.).
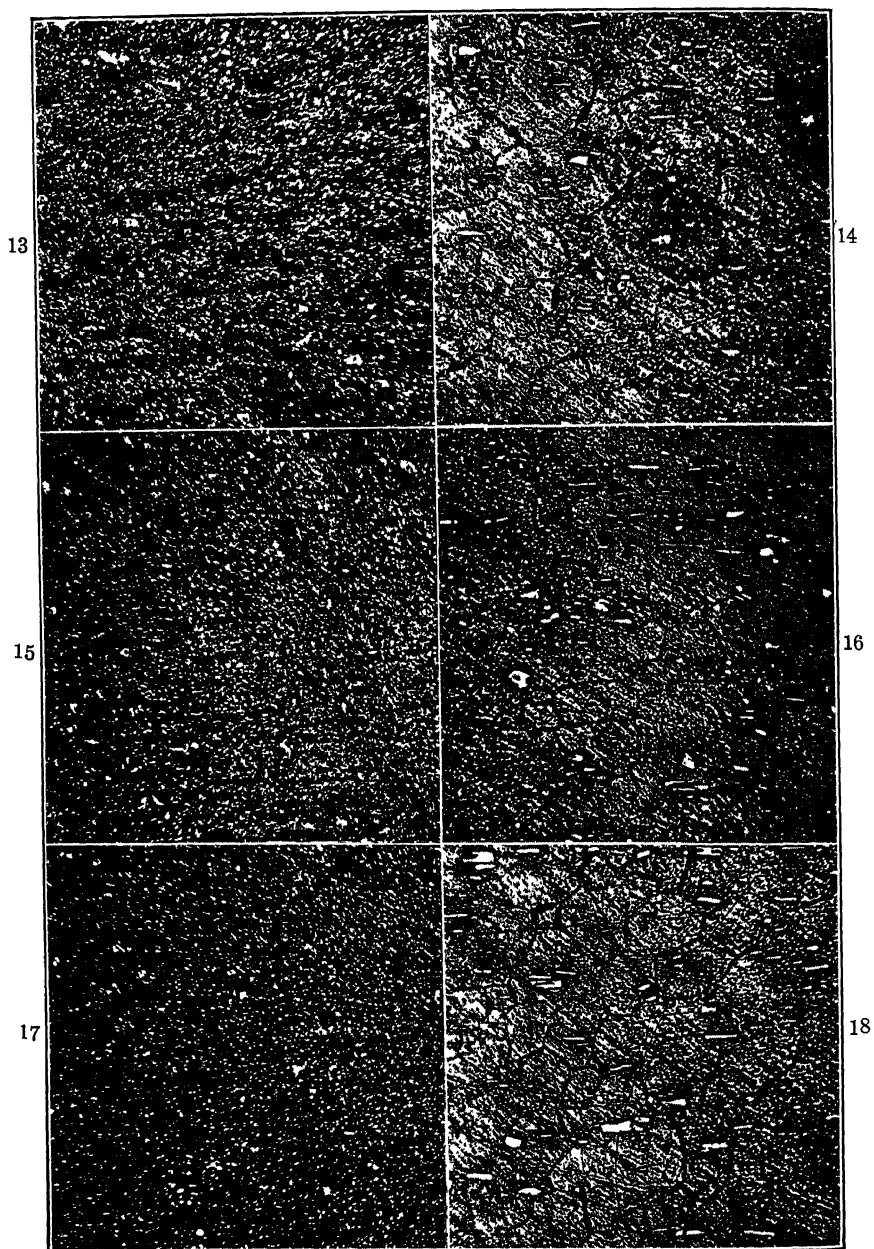
FIG. 13.—AS ROLLED.   SIZE 0.157 IN.; 79.4 PER CENT. REDUCTION.
FIG. 14.—SAME AS FIG. 13, BAKED.
FIG. 15.—AS ROLLED.   SIZE 0.076 IN.; 92.4 PER CENT. REDUCTION.
FIG. 16.—SAME AS FIG. 15, BAKED.
FIG. 17.—AS ROLLED.   SIZE 0.045 IN.; 95.5 PER CENT. REDUCTION.
FIG. 18.—SAME AS FIG. 17, BAKED.
ALL FIGURES, × 250.

During baking there also are at least two factors counteracting one another; namely, a possible reduction of cold strains greater than was obtained by the heat generated during cold deformation and the opposing tendency towards a harder metal due to a solid solution containing a higher percentage of white constituent.

Finally, it should be mentioned that the recrystallization brought about by baking must have some influence of its own; also the drafts made during cold rolling, whether heavy or light.

The white constituent is mainly a copper-tin compound, though the cubes of the antimony-tin compound can be seen in isolated spots in a few of the photomicrographs.

CONCLUSIONS

1. When cold-rolled less than 40 to 50 per cent., the metal becomes slightly harder, and it is softened by application of heat. At higher reductions, the metal behaves in a contrary manner, in that it becomes continuously and greatly softened the more it is cold-rolled. When in such a state, application of heat produces an increase in hardness and strength. (For further details regarding cold rolling to more than 50 per cent. see the previous paper by the authors.) Based on photomicrographs, a theory has been advanced for the explanation of this abnormal behavior of Britannia metal.

2. With metal that has been given a considerable cold reduction of more than 50 per cent., after baking there is a slight increase in maximum tensile strength and a considerable increase in the breaking load with corresponding loss in elongation.

3. Bend tests were performed on metal cold-rolled more than 50 per cent., by which the permanent set could be accurately determined. The baked specimens showed about twice as high an elastic limit as the unbaked specimens.

4. A slight increase in hardness was found after aging in metal cold-rolled more than 50 per cent. and in the baked metal.

5. Baking reduces somewhat the ductility of Britannia metal cold-rolled more than 50 per cent., as measured by the Erichsen machine.

ADDITIONAL REFERENCES

[3] O. W. Ellis G. B. Karelitz: A Study in Tin-base Bearing Metals. *Trans.* Amer. Soc. Mech. Engrs. (1928) **MSP50**, 11.

[4] F. Hargreaves and R. J. Hills: Work-Softening of Eutectic Alloys. *Jnl.* Inst. of Metals (1928) **40**, 41.

[5] Work-Softening and a Theory of Intercrystalline Cohesion. *Jnl.* Inst. of Metals (1929) **41**, 257.

DISCUSSION

P. D. MERICA, New York, N. Y.—There is one point that is not quite clear to me. Dr. Egeberg discusses the possibility of the precipitation of a second constituent from

the matrix of Brittania metal during working as being due possibly to the pressure of the rolls, in somewhat the same manner as martensite is precipitated from manganese steel by cold working. I wonder whether the explanation is perhaps not simply this, that at the temperature of the metal during rolling (which was above room temperature but below the baking or annealing temperature) the solubility of this constituent was less than at the baking temperature but the mobility was sufficient to enable it to crystallize out, whereas at the higher temperature this constituent was actually absorbed into solid solution.

S. EPSTEIN, Washington, D. C.—In these experiments on the hardness of cold-worked metal we should give especial consideration to the accuracy with which the Brinell hardness is measured. As the metal is cold-worked it gets thinner and thinner, and it may become a problem to measure the Brinell hardness. If the specimen gets very thin this problem is bound to arise, and I know of erroneous results that have been obtained in determining the Brinell hardness of thin sections because of the "anvil effect."

F. HARGREAVES, Ashford, Kent, England (written discussion).—I am much interested in this paper and the previous one,[6] as they concern phenomena in which I have carried out a considerable amount of work. The alloy used by the authors, when in equilibrium, consists, presumably, of the copper-tin compound and a fine eutectic groundmass. One effect of the annealing, as seen from the photographs, is to bring it more nearly into equilibrium (compare Fig. 5 with the annealed samples) and this alone will influence the hardness and structure.

The behavior under progressive amounts of work is very similar to that of the copper-tin eutectic.[7] In this case as the solubility of copper in tin is practically nil, it is evident that precipitation of an insoluble constituent cannot be a factor in the softening under heavy working. Similar remarks apply also to the behavior of the silver-tin[8] eutectic but in this case the alloy softens at all values of the amount of work. The solubility of silver in tin is under 0.1 per cent.

The increase in hardness on baking is attributed to the passing into solution of the white constituent. While this supposition is not unreasonable, there appears little evidence in the paper in its favor. It is seen from Table 4 that aging after working and annealing results in increased hardness. If the increase in hardness on baking were due to solution of the white constituent, we should expect that, in consequence of the lower solubility at room temperature, subsequent standing at this temperature, on account of reprecipitation, would result in a decrease and not an increase.

I have evidence (as yet unpublished) that solubility changes probably form an important factor in work-softening in certain cases. In other cases it does not appear to enter. For example, the cadmium-zinc eutectic[9] was reduced from Brinell hardness 33 in the as-cast condition to about 21 when heavily worked. On standing at air temperature its hardness rose again to 31. It is evident that some other factor is at work.

I consider that the explanation of work-softening phenomena generally will involve a number of distinct factors, each of which will operate to different degrees in different alloys.

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[6] B. Egeberg and H. B. Smith: Effect on Cold Rolling and Heat Treatment on Physical Properties of Britannia Metal. *Trans.* A. I. M. E., Inst. Metals Div. (1929) 373.

[7] F. Hargreaves and R. J. Hills: Work-Softening and a Theory of Intercrystalline Cohesion. *Jnl.* Inst. Metals (1929) **41**, 257.

[8] F. Hargreaves and R. J. Hills: *Idem.*

[9] F. Hargreaves and R. J. Hills: Work-Softening of Eutectic Alloys. *Jnl.* Inst. Metals (1929) **40**, 41.

G. P. DE FOREST, New York, N. Y. (written discussion).—In explanation of the change in properties that the metal undergoes when annealed after severe cold working the authors suggest that the white constituent (epsilon solid solution of copper in tin) is dissolved in the matrix to increase its hardness and strength over that of the cold-worked metal and to decrease its ductility. They indicate that the epsilon constituent, which was broken up in working, and the "precipitated" epsilon constituent form a larger part of the mass than is taken up by the same constituent after annealing, and that this is shown by the photomicrographs.

Cooling curves were run at the National Lead Co. Laboratories on a metal of the same composition and prepared under conditions similar to those described in the paper. These cooling curves, of the differential type obtained by the use of the apparatus described by Hiers and de Forest,[10] were run from well above the liquidus line to 70° C. The liquidus was found to be at 295° C. and the solidus at 244° C. Below the solidus there was no evidence of any critical points. Without apparent changes in the constituents and their proportions that are stable between 70° C. and the eutectic temperature, it seems highly improbable that under atmospheric pressure any material differences in the solubility of epsilon could exist. They may or may not, of course, exist under high pressure as in rolling.

Otherwise the changes in properties may be explained by another means indicated by the authors but less strongly stressed. This explanation is that the epsilon crystals act as keys to bond the grains of the matrix together. This explanation is consistent with the microstructure of the cast metal and its high hardness. It is consistent with the microstructure of the severely worked metal with its keys finely divided and dispersed, and its low hardness and strength with high ductility. It is finally consistent with the microstructure of the annealed metal with its increased hardness and strength and decreased ductility. Here we need to consider the microstructure more carefully, to show that by annealing the keying effect of the epsilon is restored.

The authors state that all the microsections are transverse (to the direction of rolling). This is important because, if we look well at the photomicrographs of the annealed specimens we note that the epsilon constituent presents almost entirely transverse sections of the epsilon needles. (Longitudinal sections as shown in the unworked samples, Figs. 5 and 6, are conspicuously absent.) It is to be concluded from this that the epsilon needles are consistently oriented parallel to the direction of rolling though other micrographic evidence of this is unfortunately absent. The concentration of epsilon into large crystals and into copper-tin eutectic (in the grain boundaries) may account for all the epsilon in the unannealed specimens. This is deducible from the photomicrographs on two accounts. First, the epsilon needles in transverse section show a smaller percentage of a plane section, especially in a small field, than do the more striking longitudinal sections. Secondly, we must consider the size of particles and the manner of etch. With the deep etch employed, it is reasonable that a large number of small epsilon particles (which are more resistant to the etch than the matrix) should be brought out, probably in several planes, above the groundmass of the worked metal; whereas, by deep etching, the large crystals of the annealed metal are simply brought into higher relief without any appreciable change in their quantity.

Lastly, in support of the keying argument and the suggestion that the recrystallized epsilon needles are oriented in a direction parallel to that of rolling, let us consider the differences in properties between the annealed sections tested longitudinally and transversely. There is no difference in hardness shown between samples 1L and 1T but in tensile strength 1T is higher than 1L, and in ductility it is lower. This is consistent with a greater resistance to movement across the keys than along them.

[10] G. O. Hiers and G. P. de Forest. See page 207.

B. EGEBERG AND H. B. SMITH (written discussion).—Mr. Epstein's remarks leave the impression of doubt towards the Brinell hardness figures reported by the authors. We feel that the tests have been made with such care that there should be no doubt as to the general relation between Brinell hardness, amount of cold rolling and heat treatment of the special alloy discussed. The findings have been substantiated by measurements of physical strength, which are in agreement with the Brinell figures. We agree with the remarks of Mr. Epstein in general, and though the conditions mentioned by him might have affected the accuracy of the measurements to some extent, we feel convinced that the general trend as indicated in our paper is correct.

We appreciate the remarks of Mr. Hargreaves, but we cannot entirely agree with his reasoning. In our paper, we deal with an unstable condition brought about by heat and high pressure during cold rolling of a cast alloy, which may not have been fully in equilibrium at the start, and the conversion of this by heat into a more stable form. What conditions are in equilibrium at high pressure is not known, therefore we believe our paper cannot be discussed from the standpoint of equilibrium at room temperature under ordinary pressure.

We agree with Mr. Hargreaves' opinion that a variety of factors are most likely responsible for the work-softening of certain alloys. Several of these have been mentioned in the paper and the effect of cold working and baking upon the physical properties has been attributed to the sum of these actions and not singly to the one Mr. Hargreaves has preferred to discuss.

Mr. de Forest has extended materially the theory of the keying action of the white constituent. He explains the facts put forth in our paper from the standpoint of this keying action only. Though we heartily agree to the effect of key crystals upon the physical properties, we differ somewhat as to the magnitude of this effect in the present case. Again, we believe that the facts put forth in our paper are the results of the combined effects of a variety of factors, including that of the key action. Following the thoughts outlined by Mr. de Forest, it is to be expected that the crystals of the white constituent demonstrated by the as-cast sample (Fig. 5) would cover less area in Figs. 7, 9, 11, 13, 15 and 17, showing transverse sections during various stages of cold rolling. During working, the white needles would arrange themselves longitudinally in the metal, showing only cross-sections in the transverse direction. However, the area of the white constituent seems to increase by cold rolling, indicating that other forces than the purely mechanical one mentioned by Mr. de Forest are also at work. The difference in physical properties, especially in ductility, of transverse and longitudinal test bars can be explained equally satisfactorily by other reasons than by a difference in key action. Even in alloys having but one single constituent—and therefore no key action—this variation is noted and due, for example, to coring. We do not dispute the existence of the longitudinal microstructure described by Mr. de Forest, though the restoration of the key action during baking, whereby Mr. de Forest explains the increase in hardness, would most likely have a tendency to eliminate the difference in microstructure between rolled and baked metal as far as orientation of the key crystals is concerned. We believe, therefore, that the key effect is not sufficient to explain our experimental results. In our paper there is substantial evidence, we believe, for the existence of a solubility equilibrium which has been destroyed by pressure during cold rolling, resulting in a softening and weakening of the metal. By seasoning at room temperature, this equilibrium is partly restored, resulting in some increase in hardness. This restoration is greatly favored by heat, the more so the higher the temperature, and we refer in this respect to our previous paper on the same subject.[11] Such an explanation does not necessitate any critical points between 70°C. and the solidus of the alloy, on the absence of which Mr. de Forest has rejected our

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[11] B. Egeberg and H. B. Smith: *Op cit.*

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theory of solubility. In this respect, we refer to the fact that seasoning at room temperature has an appreciable effect, though the reaction is sluggish, and a critical point, if any, would be found therefore at lower temperatures than investigated by Mr. de Forest.

We believe that the above also applies to the remarks made by Mr. Merica. According to the experiments of our previous paper, the baking of cold-rolled metal at any temperature, from room temperature up, is productive of an increase in hardness due, for one reason, to absorption of the white constituent. Following the line of thought given by Mr. Merica, a certain temperature, obtained by and during cold working of the metal in the rolls, would result in a precipitation and softening, whereas the same temperature, when applied after the cold rolling was over, would result in an absorption of the white constituent and hardening of the alloy. This is exactly what takes place according to our experiments and furnishes sufficient evidence that it is not the temperature, but the pressure, that is the main factor during rolling and that this is great enough to overshadow the opposing effect of the heat developed in the alloy when between the rolls.

Expansion Properties of Low-expansion Fe-Ni-Co Alloys

By Howard Scott,* East Pittsburgh, Pa.

INVAR is the preëminent low-expansion metal by virtue of the fact that it can be prepared with a zero coefficient of expansion at atmospheric temperature. This fact suggests that there is little room for improvement in the expansion properties of the low-expansion nickel steels. The inference is true, however, only so far as the expansion at and near atmospheric temperature is concerned, because the expansivity of invar starts to increase rapidly on heating above 100° C. and soon reaches the value of copper. Guillaume[1] met this situation by increasing the nickel content above that of invar. By that expedient, alloys having low expansivity under higher temperatures were obtained, but not without a large increase in minimum expansivity. The increase in minimum expansivity with increasing nickel content severely limits the technical applications of these alloys at high temperatures.

Prospects of improving the expansion characteristics of the nickel steels is offered by alloying. Search for an advantageous alloying addition by analogy with other alloy systems, however, is not productive because the low-expansion characteristic is unique with that system. The rule of mixtures usually gives a fair value of the expansivity of other solid-solution alloys, but in the iron-nickel systems gives a value of 18×10^{-6} per deg. C. whereas the actual value is 1×10^{-6} per deg. C. Apparently suitable additions are not to be deduced from such ingenuous considerations.

Recognition of the fact that the temperature range of low expansivity in nickel steels is terminated with loss of magnetism affords a more promising basis for the selection of an advantageous element. One may expect from that fact that additions of nonmagnetic elements to the iron-nickel alloys are detrimental to the low-expansion characteristic. Indeed, carbon, manganese, silicon, copper and chromium are detrimental to the expansion properties and no nonmagnetic element is reported to be beneficial. From the same viewpoint, the addition of a magnetic metal offers prospects of improvement. As two of the three ferromagnetic elements are already present in the

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[1] U. S. Bureau of Standards *Circular* 58 gives an excellent review of the history and properties of the low-expansion nickel steels.

low-expansion alloys, there remains only cobalt as a promising addition thereto. Brace[2] made this addition and found a marked improvement in the expansion properties.

The introduction of cobalt into the iron-nickel alloys brought complications not met in the simpler system. Investigation of these complications showed that a certain minimum content of nickel is required to preserve the low-expansion characteristic over a favorable temperature range when cobalt is present in considerable quantity. With incomplete knowledge of the limiting nickel content, a series of alloys was prepared with a high constant nickel content and cobalt variable. Study of the expansion properties of this group of alloys showed the general effects of cobalt and permitted an explicit statement of the problem of determining optimum compositions, as given in the following section. Subsequent sections are devoted to the experimental solution of the problem and to the determination of the relation of the expansion properties to composition.

The apparatus used for measuring expansion makes use of the differential expansion between the test specimen and a fused silica tube. Differential length changes are measured by means of a dial indicator sensitive to 0.0001 in. The test method has already been described[3] except for one improvement. This was the substitution of a pin bearing at the contact end of the mechanical length-change indicator for the previous ball-and-socket contact between the lever arm and the silica rod which transmits motion of the upper end of the specimen to the indicator. The readings of the length-change indicator were converted into true unit expansion by the relation:

$$E = \frac{Mx}{L} + NT$$

where E is the true unit expansion between 0° C. and the temperature of observation T. x is the corresponding increment in dial reading, L is the length of the specimen, M a correction for transverse expansion of the specimen having the value 0.95 and N a correction for the expansion of the silica tube having the value 0.53×10^{-6} per degree Centigrade.

The alloys tested were prepared by melting 13-lb. charges of electrolytic iron and nickel with other elements in a high-frequency induction furnace. The charges were melted in magnesia-lined graphite crucibles and protected from excessive oxidation by a top on the furnace. Manganese and silicon were added just before pouring. Ingots 2 in. square were poured in cast iron molds and forged usually to ⅜-in. round bars. These bars were rolled or swaged to ¼-in. dia. and were tested after annealing.

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[2] U. S. Patent 1689814.

[3] H. Scott: *Trans.* Amer. Soc. Steel Treat. (1928) **13**, 829.

EXPANSION CHARACTERISTICS

The significant expansion characteristics of the Fe-Ni-Co alloys are brought out clearly by a complete expansion curve of an alloy having insufficient nickel content to depress the gamma to alpha (Ar₃) transformation of iron, below atmospheric temperatures. Such a curve, taken through a complete cycle of heating from liquid-air temperature, about −180° C., to 780° C. and cooling again, is given in Fig. 1. It is evident that Ar₃ was consummated on the initial cooling to room temperature, after which the alloy has approximately the same expansivity (slope of curve) as ordinary steel. On the first heating Ac₃ starts at about 400° C. and progresses gradually to completion at 750° C. The alloy, now in the austenitic state, has a very high expansivity which it retains on cooling until it reaches inflection temperature (approximately 460° C.), below which its expansivity rapidly diminishes to a low value while the alloy is still in the austenitic state. At 100° C. Ar₃ starts and the reversible expansion range ends.

FIG. 1.—CONTINUOUS EXPANSION CURVE OF AN FE-NI-CO ALLOY ON HEATING FROM −180° C. TO 780° C. AND COOLING TO −180° C.

This curve shows both the low expansivity characteristic of these alloys and the A₃ transformations of iron.

It is important to recognize here that the expansion on cooling from 780° to 100° C. is reversible; i. e., if cooling is stopped above 100° C. and the specimen is again heated, the expansion curve of cooling will be retraced. If, however, the cooling is stopped below 100° C., the expansion curve of cooling is not reproduced on heating again; in other words, the expansion is irreversible. Evidently, then, it is essential to depress Ar₃ below atmospheric temperature in order to enable practical utilization of the low and reversible expansivity available on cooling between the inflection temperature and Ar₃; 460° C. and 100° C. in this case.

The alloys of immediate concern were prepared by melting charges of 32 per cent. nickel and 1 per cent. manganese with different amounts of cobalt, the remainder of the charge being iron. Their compositions are given in Table 1, together with all the compositions considered. Only one of these alloys, No. 1782, showed Ar₃ on cooling to liquid-air temperature; then it started at −130° C. (Fig. 2). Consequently the expansion properties of this group can be investigated at normal temperatures with assurance of freedom from complications introduced by the irreversible transformation of iron.

Expansion curves of members of the group concerned are given in Figs. 3 and 4. These curves were all taken on heating. Some observations were taken on cooling also, but are not plotted. The observations on cooling usually fell close to those on heating, otherwise the curves on heating were not accepted as reliable. These curves are plotted from 0° C. to well above the inflection temperature, although in most cases the curves were taken from liquid-air temperatures. This was done to show the expansion range of chief interest on a scale sufficiently open to avoid confusion. Some curves below 0° C. will be introduced later.

TABLE 1.—*Composition of Alloys*

Alloy No.	Ni, Per Cent.	Co, Per Cent.	Mn, Per Cent.	C, Per Cent.	Fe,^{a} Per Cent.
1655	28 4	9.8	0.86	0.03	60 8
1700	31 3		0.70	0.03	67.9
1708	26 6	9.9	2.30	0.05	61.2
1744	10.2		9.20	0.03	80 6
1782	31.8	6.0	0.84	0 02	61 3
1783	31 9	9 8	0.79	0.01	57 4
1784	31.9	14.2	0.85	0 01	53 1
1791	33.3		0 88	0.03	65 8
1987	31.7	16.0	0 65		51 6
1988	31.6	16 7	0.83		50.9
1989	31 6	18.6	0.78		49.0
2031	32 4	8.2	0.66		58.7
2034	32.7	11.0	0.62		55.6
2089	24.8	23 9	3.52		47.7
2090	30.5	19.0	0.81		49.6
2091	28.0	20.7	0.67	0.02	50 6
2092	26.4	23.3	0 74		49.5
2106	38.0	10.5	0.66		50 8
2113	27 4	22.1	0.69		49.8
2114	25 1	23.4	0.68	0.03	50 8
2115	24 3	24.4	0 63		50.6
2118	19.8	38.2	0.91	0.53	41.1
2119	15 2	42 6	0.93		41.2
2123	29.8	15 5	0.22		54.5
2125	28.0	17.4	0 64	0.02	54.0
2127	23.6	29.6	0.81		46.0
2146	23.4	25.4	0.35	0.14	50.7
2147			0.56	0.02	51.3
2148			0.52	0.11	51.3
2149	24.1	24.0	0.57	0.19	51.1
2150			0.61	0.33	51.0
2151	19.3	28 9	3.77		48.0

^{a} By difference.

It is now of interest to compare the expansion properties of these alloys with those of appropriate cobalt-free alloys. This may be done

by plotting as in Fig. 5, the expansion curves of selected alloys with and without cobalt having the same expansivity or temperature range
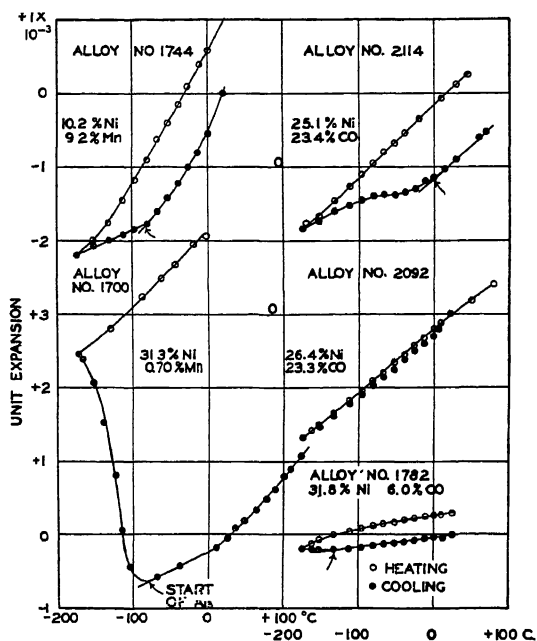
FIG. 2.—EXPANSION CURVES OF ALLOYS ON COOLING IN LIQUID AIR TO LOCATE COM-MENCEMENT OF AR_3 WHEN BELOW ATMOSPHERIC TEMPERATURE.
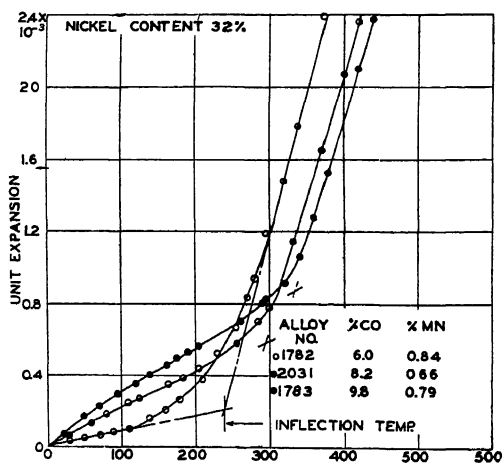
FIG. 3.—EXPANSION CURVES OF ALLOYS CONTAINING 32 PER CENT. NICKEL AND 6 TO 10 PER CENT. COBALT. AR_3 HAS BEEN DEPRESSED BELOW ATMOSPHERIC TEMPERATURES.

of low expansivity. Of two alloys having nearly the same expansivity in the low range, Nos. 1794 and 1988, that having a substantial cobalt

content, No. 1988, has a much longer range of low expansivity. In the same way, of two alloys having the same range of low expansivity, Nos. 1794 and 2034, the one having a high cobalt content, No. 2034, has much the lower expansivity over that temperature range.

The foregoing comparison is interesting but not quantitative; also, the results apply to only a single pair of alloys. To furnish a more general and useful basis for determining the effects of cobalt, it is necessary to evaluate the expansion characteristics numerically. The two properties of these alloys of chief interest are the inflection temperature
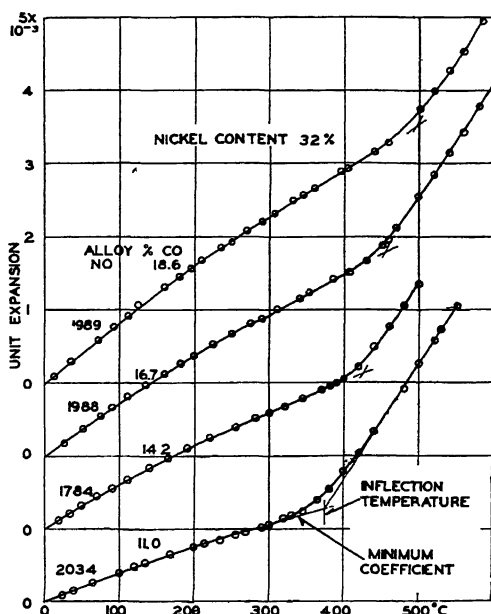
FIG. 4.—EXPANSION CURVES OF ALLOYS CONTAINING 32 PER CENT. NICKEL AND 11 TO 19 PER CENT. COBALT.

and a value representative of the expansivity below the inflection temperature. The inflection temperature may be conveniently, though arbitrarily, evaluated by the temperature of intersection of two straight lines, one drawn tangent to the curve at the point of minimum slope and the other at the point where the slope of the curve first reaches a value of about 16×10^{-6} per deg. C. The slope of the line first mentioned evidently gives the value of the minimum expansivity, a significant and useful property of the alloy. For some purposes, however, a mean value of the expansivity is more useful. For this the slope of the straight line connecting the origin and the expansion value at the inflection temperature is taken and identified as the mean expansivity.

The properties just described of the alloys containing 32 per cent. nickel are given at the top of Table 2, following the same data on cobalt-

free alloys taken from the previous report. We now have numerical values of the expansion characteristics of alloys with and without cobalt, which may be compared easily. From examination of the tabulated data, it is readily apparent that the inflection temperatures correspond closely in alloys having the same content of nickel plus cobalt whether the cobalt content is high or low. Accordingly, the expansion characteristics are plotted against nickel plus cobalt content in Fig. 6.

Referring to the inflection temperature first, plotting this property against nickel plus cobalt is fully justified because the observations for both cobalt-containing and cobalt-free alloys fall close to a smooth curve.
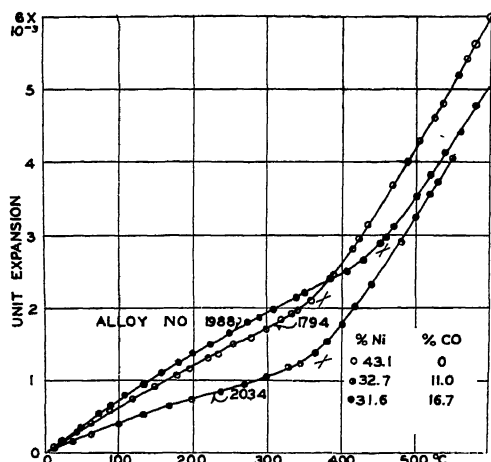
FIG. 5.—EXPANSION CURVES SHOWING EFFECT OF COBALT IN LOWERING EXPANSIVITY WHEN INFLECTION TEMPERATURE IS UNCHANGED AND IN RAISING INFLECTION TEMPERATURE FOR A GIVEN MINIMUM EXPANSIVITY.

This permits the statement of a general rule; namely, that cobalt has quantitatively the same effect on the inflection temperature as nickel. Accordingly, cobalt must be considered as a substitute for nickel rather than as an addition agent to the low-expansion nickel steels.

It may now be stated that comparison of alloys on the basis of nickel plus cobalt content is equivalent to comparison on the basis of equal temperature ranges of low expansion. That statement infers that the temperature range of low expansivity is the same for a given inflection temperature whether the cobalt content be low or high, which is supported by Fig. 5. This is the most satisfactory basis of comparison for, after all, the merit of the cobalt-containing alloys depends on the degree to which their expansivity is lower than that of cobalt-free alloys having the same temperature range of low expansivity. Consequently the difference between the curves of either minimum or mean expansivity of the cobalt-free and cobalt-containing steels is a direct measure of the improvement conferred by the substitution of cobalt for nickel.

The minimum and mean expansivities of the alloys considered are plotted against nickel plus cobalt content at the bottom of Fig. 6. In both cases the curves for the alloys containing cobalt are lower than those for the cobalt-free alloys, showing the improvement conferred by the substitution of cobalt for nickel. Moreover, the separation between

TABLE 2.—*Observed Expansion Properties of Alloys*

Alloy No.	Composition			%L″ / %Fe	Inflection Temperature Deg. C.	Expansivity	
	Ni, Per Cent.	Co, Per Cent.	Mn, Per Cent.			Minimum	Mean
NICKEL VARIABLE							
1791	33.3	<1.0	0.88		125	1.2 × 10⁻⁶	4.6 × 10⁻⁶
1717	33.8	<1.0	0.88		130	1.1	3.8
1793	35.9	<1.0	0.87		210	1.1	3.0
1819	38.2	<1.0	1.00		250	1.5	3.0
1863	40.2	<1.0	0.80		310	2.2	3.4
1864	42.1	<1.0	1.54		325	3.7	4.8
1794	43.1	<1.0	0.92		370	5.0	6.2
1718	47.1	<1.0	0.82		430	7.0	7.8
10	50.2	<1.0	0.64		510	9.1	10.0
MANGANESE VARIABLE							
1912	45.2	<1.0	0.53		420	6.1	7.0
1913	45.4	<1.0	1.96		390	6.6	7.3
1914	45.4	<1.0	5.03		325	7.4	8.2
2123	29.8	15.5	0.22		415	3.3	4.3
2125	28.0	17.4	0.64		400	3.1	4.1
COBALT VARIABLE, NICKEL CONSTANT							
1782	31.8	6.0	0.84	0.56	240	0.9	2.4
2031	32.4	8.2	0.66	0.59	295	1.7	2.6
1783	31.9	9.8	0.79	0.59	335	2.4	3.0
2034	32.7	11.0	0.62	0.62	375	3.0	4.0
1784	31.9	14.2	0.85	0.64	425	4.3	5.4
1987	31.8	16.0	0.65	0.65	450	5.0	6.0
1988	31.6	16.7	0.83	0.67	450	5.4	6.3
1989	31.6	18.6	0.78	0.69	495	6.2	7.4
COBALT VARIABLE, NICKEL + COBALT CONSTANT							
1988	31.6	16.7	0.83	0.67	455	5.5	6.3
2091	28.0	20.7	0.67	0.59	460	4.7	5.8
2092	26.4	23.3	0.74	0.58	480	5.1	6.2
2114	25.1	23.4	0.68	0.54	465	4.2	5.5
2089	24.8	23.9	3.52	0.71	390	5.3	6.2
NICKEL + COBALT VARIABLE, MAXIMUM COBALT							
1782	31.8	6.0	0.84	0.56	240	0.9	2.4
2125	28.0	17.4	0.64	0.56	400	3.1	4.1
2091	28.0	20.7	0.67	0.59	460	4.7	5.8
2092	26.4	23.3	0.74	0.58	480	5.1	6.2
2127	23.6	29.6	0.81	0.57	500	6.6	7.7
2118	19.8	38.2	0.91	0.67	620	8.0	9.3
CARBON VARIABLE							
2114	25.1	23.4	0.68	0.54	465	4.2	5.5
2147	24.1	24.0	0.56	0.50	460[a]	3.9[a]	5.4[a]
2148	24.1	24.0	0.52	0.54	470	4.2	5.6
2149	24.1	24.0	0.57	0.57	470	4.3	5.8
2150	24.1	24.0	0.61	0.61	465	4.3	5.9

[a] Observations made during cooling.

the curves increases with the nickel plus cobalt content. It follows from this observation that the improvement is more or less in proportion to the amount of cobalt substituted for nickel, because the cobalt content increases in direct ratio to the nickel plus cobalt content in both series of alloys carrying cobalt.

Having found that the reduction in expansivity conferred by the substitution of cobalt for nickel increases with the amount of the sub-
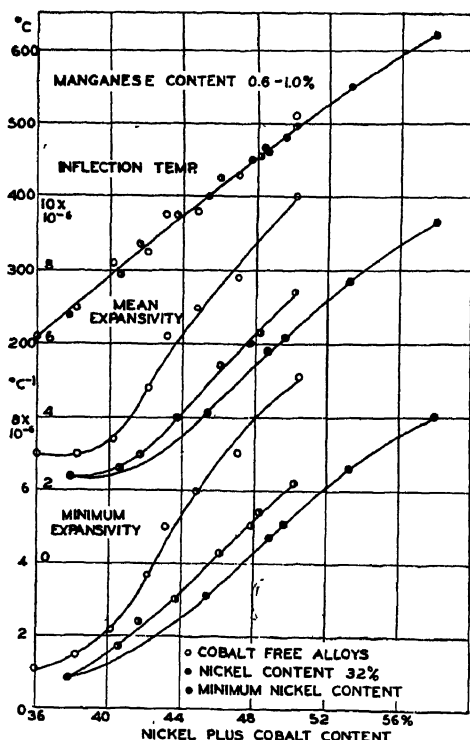
FIG. 6.—EFFECT OF NICKEL PLUS COBALT CONTENT ON INFLECTION TEMPERATURE AND EXPANSIVITY OF FE-NI-CO ALLOYS UNDER THREE DIFFERENT RELATIONS OF NICKEL TO COBALT CONTENT.

stitution, it is evident that the limit of the improvement has not been reached in this group of alloys. All of the alloys except No. 1782 will permit a considerably higher substitution of cobalt without bringing Ar_3 in the vicinity of atmospheric temperatures. This introduces the question: what is the limiting amount of cobalt that can be substituted for nickel without bringing Ar_3 dangerously close to atmospheric temperature for all useful nickel plus cobalt contents? An answer to this question is necessary to establish optimum compositions of these alloys and is sought in the following section.

LIMITING COMPOSITIONS

If iron, nickel and cobalt were the only elements present in the alloys studied, the problem of finding the optimum compositions would be comparatively simple. It is necessary, however, to add manganese and silicon to these alloys when melted in an air atmosphere to render them easily forgeable. Carbon also is always present, being introduced with the charge or picked up from the furnace atmosphere during melting. Silicon is added in such small quantities that it has no considerable effect either on the expansion properties or on Ar₃ and consequently may be neglected. Carbon and manganese, however, have pronounced effects which require evaluation.

The presence of manganese or carbon in the Fe-Ni-Co system complicates the problem because it removes these alloys from the ternary class, which can be easily represented graphically, and into the quaternary class, which cannot be so represented. This complication, however, can be avoided provided that the content of secondary elements is small, as is true of the useful alloys. The expedient applicable for this purpose is to consider manganese and carbon multiplied by appropriate factors as equivalent to nickel as regards their effects on Ar₃. Thus these complex alloys are brought into the ternary class by taking the equivalent nickel content as one composition variable.

The effect of manganese in lowering Ar₃ may be evaluated from the fact that Ar₃ starts at −80° C. in both of two Fe-Ni-Mn alloys, which differ markedly in manganese content. Their expansion curves on cooling in liquid air are given in Fig. 2 and compositions in Table 1. As the ratio of their difference in nickel content to their manganese content is 2.5, it is evident that manganese is 2.5 times as effective as nickel in lowering Ar₃. Hence the equivalent nickel content can be expressed by:

$$\% \, L' = \% \, \mathrm{Ni} + 2.5 \, (\% \, \mathrm{Mn})$$

in the absence of carbon. Lacking cobalt-free alloys in which carbon is variable, the determination of the relative effect of carbon is deferred. For the present only the relation of equivalent nickel content to Ar₃ in the practical absence of cobalt and carbon will be considered.

Plotting the data of Hanson and Hanson[4] and of the writer on the start of Ar₃ in Fe-Ni-Mn alloys against equivalent nickel content in Fig. 7, it may be seen that Ar₃ is depressed to −100° C. when the equivalent nickel content is 34 per cent. At that temperature Ar₃ is safely depressed so far as terrestrial temperatures are concerned, so this is a good value to aim at. In the series of Fe-Ni-Co alloys already considered, Ar₃ is depressed below −180° C., so higher cobalt contents can be

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[4] *Jnl.* Iron and Steel Inst. (1920) **102**, 39.

safely used. Consequently the cobalt contents with which Ar_3 is depressed to $-100°$ C. is sought for all useful nickel plus cobalt contents.

Without any preëxisting information as to the location of Ar_3 in high-cobalt alloys, a preliminary survey of this field was made to avoid nonproductive expansion tests. The compositions with which Ar_3 is depressed below atmospheric temperature, about 25° C., can be determined by any test that distinguishes between the gamma state (Ar_3 below 25° C.) and the alpha state (Ar_3 above 25° C.) at ordinary temperatures. The quick Rockwell hardness test distinguishes between these states when the compositions compared are not greatly different. The use of a
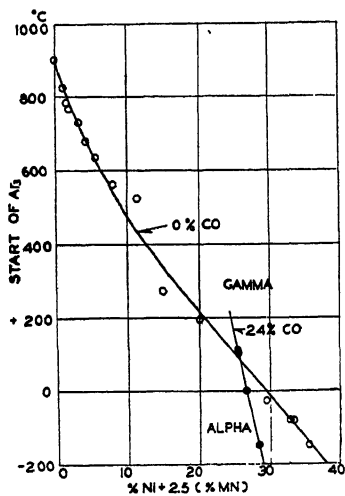
FIG. 7.—TEMPERATURE OF START OF Ar_3 IN FE-NI-CO-MN ALLOYS PLOTTED AGAINST EQUIVALENT NICKEL CONTENT.
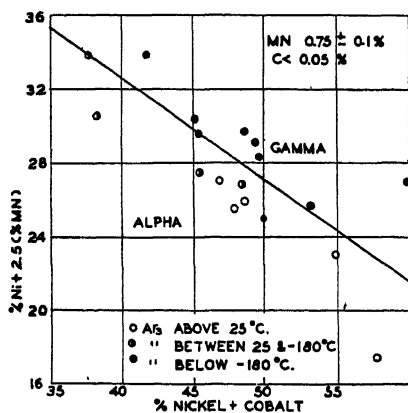
FIG. 8.—VARIATION OF MINIMUM PERMISSIBLE EQUIVALENT NICKEL CONTENT WITH NICKEL PLUS COBALT CONTENT AS ESTABLISHED BY HARDNESS TESTS.

supplemental reference temperature below atmospheric—that of liquid air—increased the definiteness and effectiveness of this test decidedly.

The results of hardness tests made to determine the constitution of the alloys containing cobalt are given in Table 3. The specimens were strips prepared by cold-rolling followed by annealing. The hardness of these strips was measured, then they were cooled to liquid-air temperature and held for 1 min. The hardness was again measured on return to 25° C. Higher hardness following cooling in liquid air shows that Ar_3 has progressed between $+25$ and $-180°$ C. This observation and the relative hardness of the alloys permitted their classification according to the location of Ar_3 in three temperature ranges, as given in Table 3.

The minimum equivalent nickel content can now be approximately evaluated as a function of nickel plus cobalt content, for a given manga-

ñese content, by plotting the former variable against the latter and indicating the temperature range in which Ar₃ occurs, by the symbol plotted, as is done in Fig. 8. A curve may now be drawn to represent the compositions in which Ar₃ occurs between $+25$ and $-180°$ C. Such a curve gives fair values of the minimum safe equivalent nickel content for

TABLE 3.—*Location of Ar₃ as Determined by Hardness Tests*

Alloy No.	Co, Per Cent.	L', Per Cent.[b]	C, Per Cent.	Rockwell B Hardness		Temperature[c] of Ar₃
				Annealed	After Liquid-air Treatment	
% Ni + Co = 45						
2123	15.5	30.3		83	82	●
2124[a]	18	27.5		92	102	◖
2125	17.4	29.6	0.02	83	94	●
2126	20	27		104	107	○
% Ni + Co = 49						
2106	10.5	39.6		76	77	●
2113	22.1	29.1		76		●
2114	23.4	26.8	0.03	80	95	◖
2115	24.4	25.9		85	101	○
2107[a]	25	25		106	107	○
% Ni + Co = 53						
2127	29.6	25.7		83	84	●
2128[a]	32	23		101	104	○
% Ni + Co = 58						
2116	0	60		76	75	●
2117	33	27		79	78	●
2118	38.2	22.1	0.53	89	89	●
2119	42.6	17.5		104	114	○
% Ni + Co = 50						
2131[a]	35	15	0.3	112	112	○
2137[a]	30	20	0.4	117	117	○
2138[a]	30	20	0.5	115		○
2142[a]	28	22	0.2	112	112	○
2146	25.4	24.2	0.14	97	113	◖
% Ni = 24.1						
2147	24.0	25.5	0.02	104	105	○
2148	24.0	25.4	0.11	96	111	◖
2149	24.0	25.5	0.19	97	105	●
2150	24.0	25.6	0.33	96	99	●

[a] Composition from charge.

[b] % L' = % Ni + 2.5 (% Mn).

[c] ○ = Ar₃ above 25° C.

◖ = Ar₃ between 25° C. and −180° C.

● = Ar₃ below −180° C.

the major portion of the system when the manganese content is about 0.75 per cent.
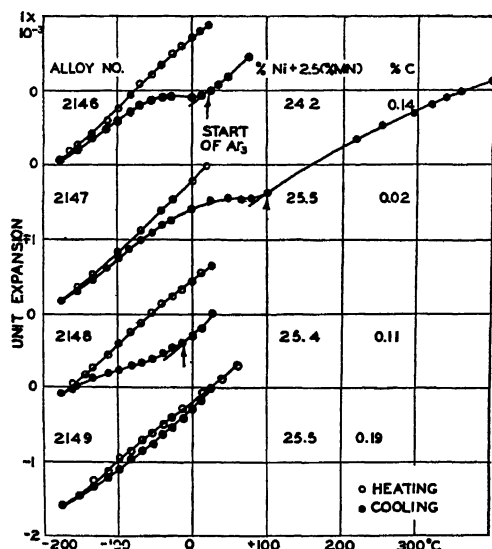
FIG. 9.—EXPANSION CURVES OF ALLOYS ON COOLING IN LIQUID AIR, SHOWING EFFECT OF CARBON CONTENT ON AR₃.

The type of observations just described furnished the initial data required, but does not permit the exact evaluation of the effect of composition variables on the maximum feasible cobalt content. For this purpose the exact location of Ar_3 is required and was determined from expansion curves taken during cooling in liquid air and heating thereafter. The significant curves obtained are plotted in Figs. 2 and 9 and reduced data from these and other curves are given in Table 4. The beginning of Ar_3 is identified by an arrow on the curves. This identification takes cognizance of the expansion-curve loop between heating and cooling on immersion in liquid air. The magnitude of this effect can be noted on the curves of alloys 2149 and 2092, which show no Ar_3 and consequently would be identical on heating and cooling were there no temperature lag between the specimen and thermocouple.
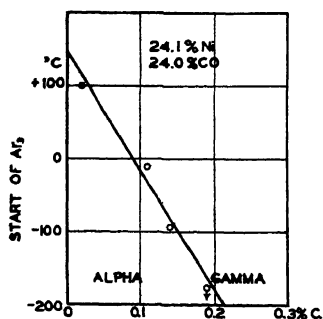
FIG. 10.—TEMPERATURE OF START OF AR₃ AS A FUNCTION OF CARBON CONTENT; NICKEL, COBALT AND MANGANESE CONTENTS CONSTANT.

Sufficient data are now available to show the position of Ar_3 at low temperatures in the presence of 24 per cent. Co as a function of nickel

content (Fig. 7) and of carbon content (Fig. 10). As the cobalt content is practically the same in both groups of alloys, the effect of carbon relative to nickel may be evaluated. The ratio of the slope of the curve for nickel variable to that for carbon variable gives the value desired, which is 18. Hence the equivalent nickel content is completely defined by:

$$\% L'' = \% \text{ Ni} + 2.5(\% \text{ Mn}) + 18(\% \text{ C})$$

This expression, however, is significant only with low carbon contents because dissolved carbon alone lowers Ar_3. Free carbon, either as carbide or graphite, obviously has no effect on the position of Ar_3.

TABLE 4.—*Location of Ar_3 as Determined by Expansion Tests*

Alloy No.	Co, Per Cent.	L″, Per Cent.[a]	$\frac{\%L''}{\%Fe}$	Start of Ar_3	
				Temperature Deg. C.	Symbol[b]
1700	0	33.6	0.49	− 80	◖
1744	0	33.7	(9.2% Mn)	− 80	◖
1791	0	36.0	0.55	−175	●
1655	9.8	31.1	0.51	+ 25	◖
1782	6.1	34.3	0.56	−130	◖
1783	9.8	34.1	0.59	−175	●
1784	14.2	34.2	0.64	−175	●
1988	16.7	33.9	0.67	−175	●
2091	20.7	29.9	0.59	−175	●
2113	22.1	29.3	0.59	−175	●
2092	23.3	28.5	0.58	−175	●
2114	23.4	27.3	0.54	0	◖
2147	24.0	25.9	0.50	+100	◖
2148	24.0	27.4	0.54	− 10	◖
2149	24.0	28.9	0.57	−175	●
2146	25.4	26.7	0.53	+ 25	◖
2146	24.0	28.0	0.55	− 90	◖

[a] $\% L'' = \% \text{ Ni} + 2.5 (\% \text{ Mn}) + 18 (\% \text{ C})$.
[b] ◗ = Ar_3 above 25° C.
◖ = Ar_3 between 25° C. and −180° C.
● = Ar_3 below −180° C.

The solid solubility of carbon in the high-cobalt alloys was estimated from chemical determinations of total and graphitic carbon. Two alloys containing 0.53 and 0.33 per cent. total carbon gave 0.19 and 0.01 per cent. graphitic carbon respectively. Accordingly, the solid solubility of

carbon in these alloys is about 0.30 per cent. A greater content may be kept in solid solution with higher total contents, provided that the metal be cooled rapidly from a high temperature and not reheated beyond 400° C. thereafter. This is shown by the expansion curve of the 0.53 per cent. carbon alloy given in Fig. 11. On the first heating of this alloy after rapid cooling from the annealing temperature, an irreversible contraction starts at 460° C. and continues to 640° C. Evi-
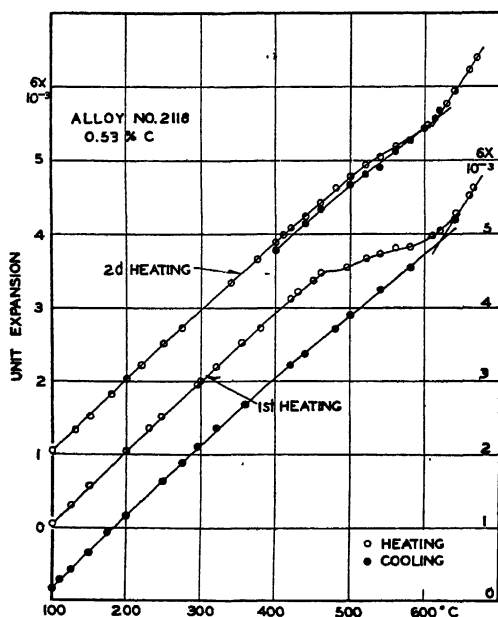
FIG. 11.—EXPANSION CURVES OF HIGH-CARBON ALLOY, SHOWING CONTRACTION CAUSED BY PRECIPITATION OF CARBON.

dently this contraction is due to the precipitation of carbon as graphite from solid solution.

With the foregoing information, it is possible to give the maximum permissible cobalt content for these alloys. This might be done graphically as in Fig. 8, which applies for a manganese content of 0.75 per cent., carbon nil, but a different curve would be required for each manganese and carbon content. Fortunately such a cumbersome representation is not necessary. Certain fundamental considerations revealed a simple means for accomplishing the same thing developed in the following digression.

According to the curves for the carbon-free alloys, it appears that cobalt has a decided effect in lowering Ar₃. This is clearly shown by the equivalent nickel contents required to depress Ar₃ to −100° C. in the

absence and in the presence of cobalt. The content is 34 per cent. in the absence of cobalt and 28 per cent. in the presence of 24 per cent. Co. This effect is apparently anomalous because cobalt is known to have the reverse effect in Fe-Co alloys. Analysis of the problem, however, shows that the anomaly results from improper representation of the data.

If a hypothetical element which has no effect on Ar_3 should be introduced into an Fe-Ni alloy, without change in the ratio of nickel to iron, Ar_3 should remain at the same temperature. The nickel content, in that event, as normally expressed in percentage of the total weight, will be lower than without the inert addition. Consequently the nickel
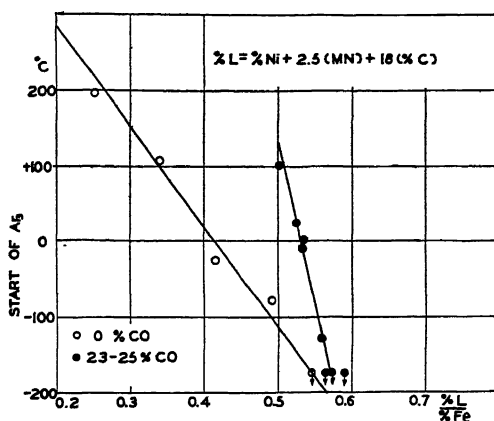
FIG. 12.—TEMPERATURE OF START OF Ar_3 AS FUNCTION OF RATIO OF EQUIVALENT NICKEL CONTENT TO IRON CONTENT OF FE-NI-CO-MN-C ALLOYS.

content should be given in terms of the iron content, to retain the characteristic effects of nickel in the presence of the inert element. If the added element is not inert, its characteristic effect on iron in the presence of nickel is revealed.

Applying the foregoing proposition to the present case, where cobalt takes the place of the inert element, Fig. 12 was prepared. Here Ar_3 is plotted against the ratio of the equivalent nickel content to the iron content for alloys containing 0 and 24 per cent. Co. So represented, Ar_3 is higher in the presence of cobalt than in its absence with high nickel contents just as in the absence of nickel. It therefore appears that the characteristic effect of one component of a ternary solid-solution alloy on the base metal is not obscured by the third component when the content of the first component is expressed in terms of the weight of base metal.

Further information of the validity of this principle is supplied by comparing the effect of cobalt in the presence and absence of nickel.

From Table 4 the following values were estimated for a constant ratio of effective nickel content to iron content of 0.55:

Co Content in Per Cent. of Fe Content	Start of Ar₃	
	In Fe-Co Alloys,[a] Deg. C.	In Fe-Ni-Co Alloys, Deg. C.
0	880	−180
16	920	−120
47	960	− 90

[a] Data from Ruer and Kaneko: *Ferrum* (1913) **2**, 34.

Thus Ar₃ is raised by cobalt to the same degree in the presence of a high nickel content as in its absence when the cobalt content is expressed in percentage of the iron content. Such a treatment should also simplify the analysis of changes in physical properties of other complex iron-base alloys with composition when the relations are not linear.

One may take advantage of this principle to express the maximum permissible cobalt content of the quinternary alloys in a simple manner. From Fig. 12 a value of the ratio of equivalent nickel content to iron content may be picked with which Ar₃ will fall safely below atmospheric temperatures. Thus for a value of the ratio of 0.55, Ar₃ will occur between about −80° and −180° C. for a range of useful compositions. That is to say, Ar₃ is safely depressed when:

$$\frac{\% \, Ni + 2.5(\% \, Mn) + 18(\% \, C)}{\% \, Fe} = 0.55 \qquad [1]$$

Substituting for the iron content, 100 minus the content of the other components and transposing:

$$\% \, Co = 100 - 2.82(\% \, Ni) - 5.5(\% \, Mn) - 34(\% \, C) \qquad [2]$$

This relation gives a fair value of the maximum feasible cobalt content in terms of components, which normally would be determined analytically.

A much more useful expression can be obtained by substituting inflection temperature for nickel content, because usually the maximum cobalt content permissible with a given temperature range of low expansivity is desired. To obtain this expression it is necessary to determine the relation between inflection temperature and composition. From Fig. 6 it is evident that the inflection temperature varies linearly with the nickel plus cobalt content when the manganese content is 0.75 per cent. and carbon content nil. In this case the inflection temperature θ in degrees Centigrade may be expressed by:

$$\theta = 19.5(\% \, Ni + \% \, Co) - 450 \qquad [3]$$

Manganese and carbon may also affect the inflection temperature. The inflection temperature is plotted against manganese content for 45 per cent. Ni and against carbon content for 24 per cent. Ni and 24 per cent. Co in Fig. 13 to show their effects. Carbon has a negligible influence on the inflection temperature, but that of manganese is important. The slope of the curve for manganese variable shows the inflection temperature to be lowered 22° C. for each per cent. of increase in manganese content. Assuming that manganese has the same effect.
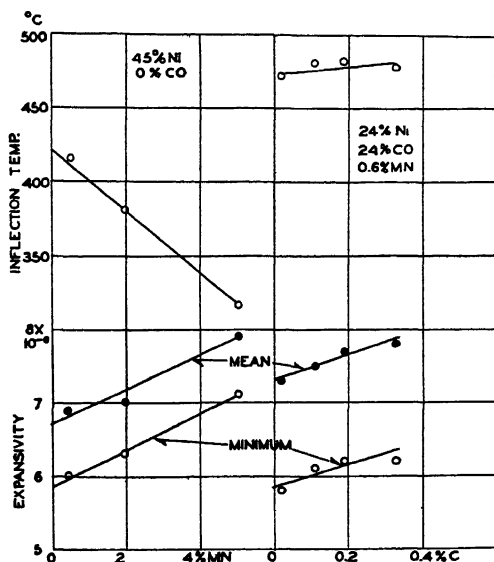
FIG. 13.—EFFECTS OF MANGANESE AND CARBON CONTENT ON EXPANSIVITY AND INFLECTION TEMPERATURE.

in the presence of cobalt, the inflection temperature may be completely expressed by:

$$\theta = 19.5(\% \text{ Ni} + \% \text{ Co}) - 22(\% \text{ Mn}) - 465 \qquad [4]$$

for the range of composition having low expansivity. Combining this relation with the preceding one to eliminate nickel gives:

$$\% \text{ Co} = 0.0795\theta + 4.8(\% \text{ Mn}) + 19(\% \text{ C}) - 18.1 \qquad [5]$$

which is the relation desired. The corresponding nickel content may be found in the same way to be:

$$\% \text{ Ni} = 41.9 - 0.0282\theta - 37(\% \text{ Mn}) - 19(\% \text{ C}) \qquad [6]$$

The equations just derived define completely the best compositions for any inflection temperature between 200° and 600° C. and for any assigned value of manganese and carbon content. To use them it is evidently necessary first to choose a value of the inflection temperature

from a consideration of the particular application problem at hand. Values of the manganese and carbon contents may then be chosen on the basis of metallurgical requirements. The nickel and cobalt contents required to give the best expansivity under these limitations with Ar₃ safely depressed are then given by equations 5 and 6.

The equations just discussed indicate that the cobalt content must be increased with the manganese and carbon contents in order to keep the .inflection temperature constant. It might be inferred that addition of manganese or carbon, or both, will permit improvement of the expansion properties by virtue of the larger additions of cobalt then feasible. This is true, however, only if the addition of either manganese or carbon raises the expansivity less than the corresponding increment of cobalt lowers it, assuming that the inflection temperature is maintained constant. The determination of whether or not advantage is to be gained by increasing manganese or carbon requires, therefore, an evaluation of their effects on the expansion properties. The quantitative determination of the effects of composition on expansivity will be considered in the following section.

ESTIMATION OF OPTIMUM EXPANSIVITY

The estimation of the best expansion properties available in the Fe-Ni-Co-Mn-C system for any particular application requiring low expansivity has been stated to be the chief objective of this investigation. This objective could be accomplished by graphical methods alone, but would entail excessive experimental effort because a large number of tests of alloys melted precisely to intended compositions would be required. Consequently an attempt was made to determine the laws of variation of the expansion properties with composition in the hope that they would lead to simple and general mathematical expressions for these relations from which the best properties could be estimated.

One step in the direction indicated was made in the last section and consisted of putting the relation between inflection temperature and composition in the form of equation 4. The existence of this and other simple relations, however, is contingent on the effects of each of the several composition variables being additive; i. e., independent of the quantity of other components present. The additive principle just stated usually applies for moderate composition changes in solid-solution alloys and Fig. 6 indicates that it governs the inflection temperature so far as cobalt is concerned. It is probable that this principle applies to the expansivity, therefore the effects of the several composition variables were investigated with the object of testing its validity.

The effects of manganese on the expansion properties were evaluated from the data on cobalt-free 45 per cent. nickel alloys given in a previous

paper[5] and are plotted in Fig. 13.   The effect of carbon was determined
from a group of high-cobalt alloys in which carbon alone was varied.
Expansion curves of this group are given in Fig. 14.   Serious irregulari-
ties in the quantities of components other than carbon were avoided by
casting several small ingots from the same melt following successive
additions of carbon.   The expansion properties are plotted against
carbon content in Fig. 13.
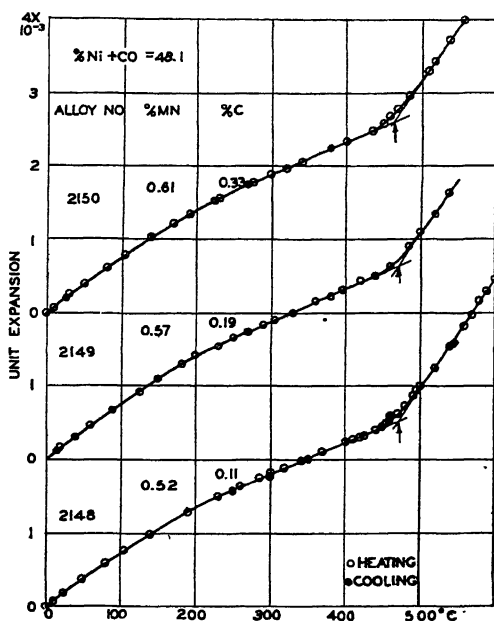
FIG. 14.—EXPANSION CURVES OF ALLOYS DIFFERING ONLY IN CARBON CONTENT.

Having determined the effects of the most troublesome variables,
the precise evaluation of the effect of cobalt becomes possible.   It is
desirable, however, to have more information on the expansion properties
of high-cobalt alloys than is obtainable with the 32 per cent. nickel series.
Consequently several new groups of alloys were prepared.   The expan-
sion curves of one group in which cobalt is the variable and the nickel
plus cobalt content constant are given in Fig. 15.   Curves of a group
having nearly the same minimum equivalent nickel content with cobalt
variable are given in Fig. 16 and of a group having widely different
manganese contents in Fig. 17.   They supply comprehensive data
which have been reduced to give Table 2 with which to work out the laws
governing the variation of properties with composition.

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[5] H. Scott: *Op. cit.*

The relation of the expansion properties to the cobalt content may now be examined without interference from the secondary variables,
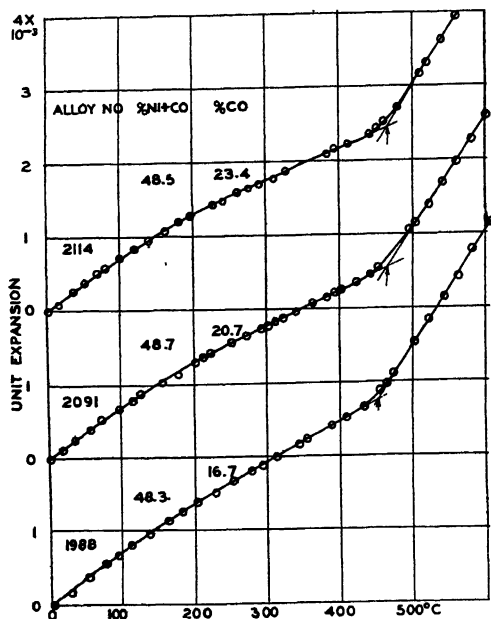
FIG. 15.—EXPANSION CURVES OF ALLOYS HAVING DIFFERENT COBALT CONTENTS BUT SAME CONTENT OF NICKEL PLUS COBALT.

manganese and carbon, by adjusting the observed property values to zero content of those elements on the basis of Fig. 13, as given in Table
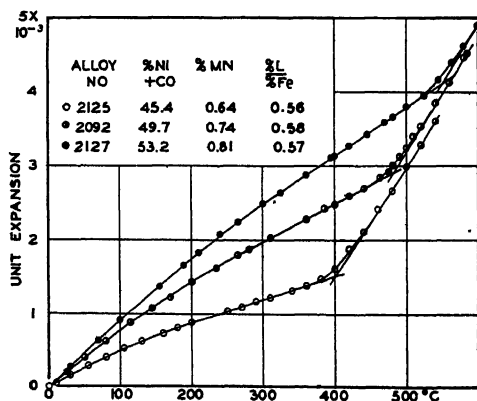
FIG. 16.—EXPANSION CURVES OF ALLOYS HAVING MINIMUM PERMISSIBLE EQUIVALENT NICKEL CONTENT, BUT DIFFERENT CONTENT OF NICKEL PLUS COBALT.

5. In some cases the values are unattainable in fact because the nickel content is so low that Ar_3 would occur above atmospheric temperature in

the absence of manganese and carbon, but this situation does not detract from their utility in their intended application, which is the establishment of basic relations.

TABLE 5.—*Effect of Composition Variables on Expansion Properties*
Expansion Data Are Adjusted for Deviation of Actual Composition from Those Given

Alloy No.	Per Cent. Variable	Inflection Temperature, Deg. C.	Expansivity		Merit Index	
			Min.	Mean	Min.	Mean
	MANGANESE VARIABLE; 0% Co, 0% C					
1912	45.0 Ni, 0.53 Mn	417	6.0×10^{-6}	6.9×10^{-6}	245	220
1913	45.0 Ni, 1.96 Mn	381	6.3	7.0	201	181
1914	45.0 Ni, 5.03 Mn	316	7.1	7.9	113	90
1794	43.1 Ni, 0.92 Mn	370	5.0	6.2	227	193
1864	42.1 Ni, 1.54 Mn	325	3.7	4.8	219	188
	NICKEL VARIABLE; 0% Co, 0% Mn, 0% C					
1863	40.2 Ni	327	2.0	3.2	270	236
1864	42.1 Ni	357	3.3	4.4	263	231
1794	43 1 Ni	389	4.8	6.0	252	218
1912	45.2 Ni	431	6.0	6.9	259	234
1718	47.1 Ni	447	6.8	7.6	253	230
10	50.2 Ni	523	9.0	9.9	266	240
	COBALT VARIABLE; 0% Mn, 0% C					
1783	9.8 Co, 31.9 Ni	352	2.2	2.8	289	272
2034	11.0 Co, 32.7 Ni	388	2.9	3.9	305	277
1784	14.2 Co, 31.9 Ni	443	4.1	5.2	326	294
1987	16.0 Co, 31.8 Ni	464	4.8	5.8	327	298
1988	16.7 Co, 31.6 Ni	467	5.2	6.1	318	293
1989	18.6 Co, 31.6 Ni	511	6.0	7.2	340	305
	Ni + Co VARIABLE; MAXIMUM Co, 0% Mn					
2123	29.8 Ni, 15.5 Co	420	3.3	4.3	326	297
2125	28.0 Ni, 17.4 Co	413	3.0	4.0	327	299
2114	25.1 Ni, 23.4 Co	480	4.0	5.3	365	328
2091	28.0 Ni, 20.7 Co	474	4.5	5.6	345	314
2092	26.4 Ni, 23.3 Co	496	4.9	6.0	356	324
2127	23.6 Ni, 29.6 Co	567	6.4	7.5	384	353
2118	19.8 Ni, 38.2 Co	640	7.8	9.1	417	380
2089	24.8 Ni, 23.9 Co	464	4.5	5.4	335	310
	CARBON VARIABLE; 0% Mn, 24.0% Co					
2114	0.03 C, 25.1 Ni	492	4.3	5.6	369	332
2147	0.02 C, 24.1 Ni	472[a]	3.8[a]	5.3[a]	363	320
2148	0.11 C, 24.1 Ni	481	4.1	5.5	364	324
2149	0.19 C, 24.1 Ni	482	4.2	5.7	362	319
2150	0.33 C, 24.1 Ni	478	4.2	5.8	358	312
2114	0.03 C, 24.1 Ni	472	3.6	4.9	369	332
	MANGANESE VARIABLE; 0% Co, 0% C					
2123	0.22 Mn				259	230
2125	0.64 Mn				242	213
2114	0.68 Mn				251	214
1988	0.83 Mn				231	208
2089	3.52 Mn				143	117

[a] Observations taken during rapid cooling.

Both the expansivity and inflection temperature vary in the same manner with the nickel content, or with the nickel plus cobalt content
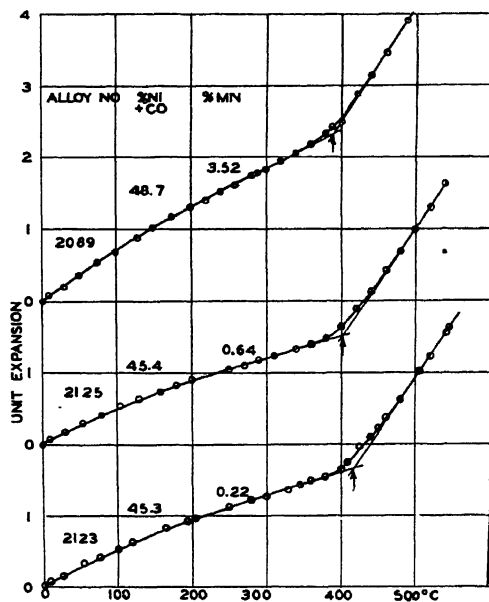
FIG. 17.—EXPANSION CURVES OF ALLOYS DIFFERING CONSIDERABLY IN MANGANESE CONTENT.
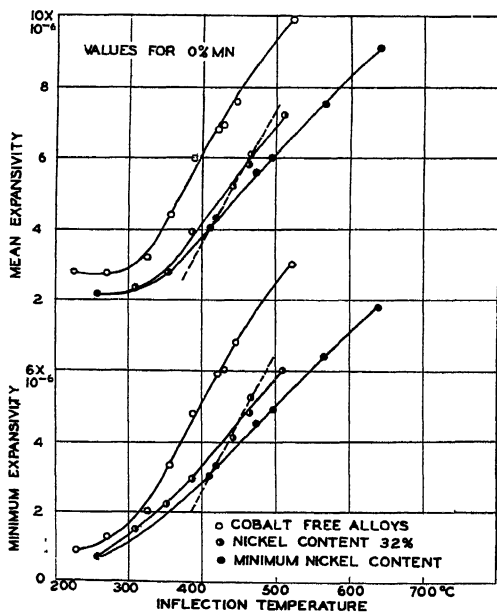
FIG. 18.—VARIATION OF MINIMUM AND MEAN EXPANSIVITY WITH INFLECTION TEMPERATURE.

For three relations between cobalt and nickel contents as estimated for zero manganese content. Broken lines apply for alloys containing constant cobalt content of 16 to 17 per cent.

when the cobalt content is a linear function of it, and this suggests plotting one property against the other, as in Fig. 18, to eliminate nickel as a variable. It is now apparent that the expansivity varies linearly with the inflection temperature over a useful range of compositions under the conditions specified. The inflection temperature varies linearly with nickel plus cobalt content, hence the expansivity must do likewise. Furthermore, from the relation of cobalt content to nickel plus cobalt content, it may be concluded that the change of the expansion properties with cobalt content is linear. Consequently the relations of these properties to composition can be expressed for a limited range of compositions by mathematical equations of the simplest form.

The curves of Fig. 18 are expressed by the equation:

$$\alpha = A(\theta - B) \qquad [7]$$

where α is the expansivity, θ the inflection temperature, and A and B are constants when the inflection temperature comes between 350° and 500° to 600° C. For the simplest case, cobalt zero, the constant A may be evaluated from the slope of the curves. Accordingly:

$$A = A_1 = A_2 = 0.035 \times 10^{-6}$$

where A_1 is the value for the minimum expansivity α_1 and A_2 the value for the mean expansivity α_2. The corresponding values of B are given by the value of the inflection temperature at which the linear portions of the curves for zero cobalt alloys extended have zero expansivity, whence: $B_1 = 262°$ C. and $B_2 = 232°$ C.

Having obtained and evaluated an equation for expansivity in terms of inflection temperature of Fe-Ni alloys, the next step is to introduce terms to express the effects of other components of the complex alloys. It has already been shown that the effect of cobalt also can be easily expressed and this may be verified by connecting the plotted values for two alloys having the same cobalt content, 16 to 17 per cent., but different nickel contents by a straight line, the broken line of Fig. 18. This line has practically the same slope as the curve for the alloy of zero cobalt content, consequently the intercept of the linear portion of the curve, which determines the value of the constant B, is in this case changed by the addition of 16 to 17 per cent. Co, but the slope, which determines the value of the constant A, is not altered. It is assumed, therefore, that the effects of manganese and carbon also are reflected in the value of B only.

The foregoing assumption affords a useful basis for expressing the merit of an alloy from its expansion characteristics alone. Transposing equation 7:

$$B = \theta - \frac{\alpha}{A} = \theta - \frac{\alpha \times 10^{+6}}{0.035} \qquad [8]$$

it is evident that the value of B will decrease as the expansivity increases or the inflection temperature decreases. Consequently the value of B
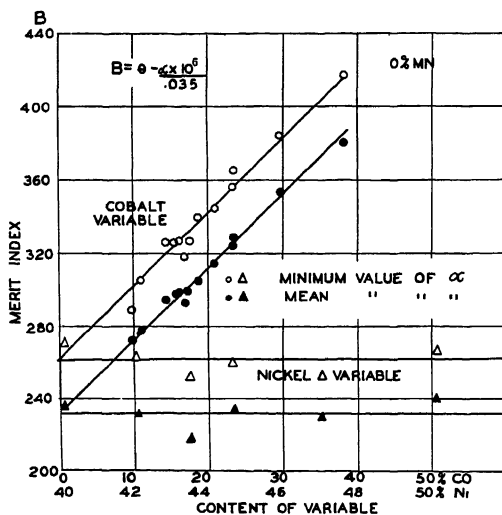
FIG. 19.—VARIATION OF MERIT INDEX WITH NICKEL AND COBALT CONTENT, OTHER ELEMENTS CONSTANT.
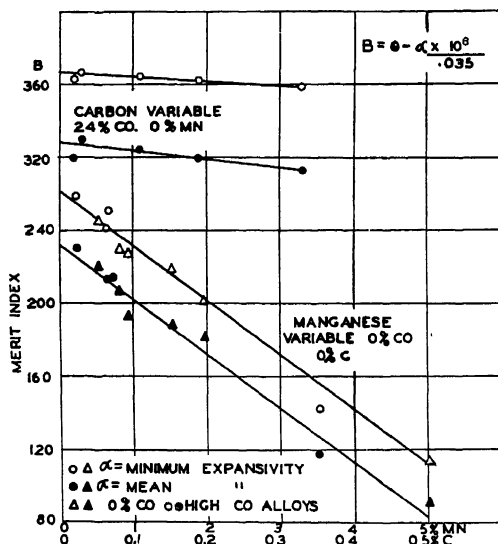
FIG. 20.—VARIATION OF MERIT INDEX WITH MANGANESE AND CARBON CONTENT, OTHER ELEMENTS CONSTANT.

is a direct measure of the merit of an alloy as long as the inflection temperature comes within the limits previously mentioned. As this single characteristic value for an alloy finds considerable use as a quantitative

measure of the effects of alloying additions to Fe-Ni alloys, it is designated "merit index" to facilitate further discussion.

The merit indices of all the alloys studied, as obtained by equation 8, are given in Table 5. Plotting the values of this property against the several composition variables gives Figs. 19 and 20. Here the value for nickel variable is constant, as required by equation 7. Cobalt has a decided beneficial effect, manganese is harmful and the effect of carbon is slight. To show the effect of manganese in the high-cobalt alloys, their merit index values are adjusted to 0 per cent. Co on the basis of the curve for cobalt variable. The fact that the values thus obtained fall on the same curve as do those for alloys actually free from cobalt verifies the previous conclusion that the effect of cobalt is additive. The same is true of manganese also, otherwise there would be considerable scatter of the points for cobalt variable, because they represent alloys of which the manganese contents differ considerably. Whether or not the additive principle holds for carbon is immaterial because the effect of this element in allowable percentages is very small.

These simple relations between merit index and composition enable the formulation of convenient mathematical expression for expansion properties as a function of composition. These relations take the forms:

$$\alpha_1 = A(\theta - B_1 + C_1Y + D_1Z + E_1W) \qquad [9a]$$
$$\alpha_2 = A(\theta - B_2 + C_2Y + D_2Z + E_2W) \qquad [9b]$$

where C, D and E are constants and Y, Z, and W are the cobalt, manganese and carbon contents respectively in percentages of total weight of alloy. Putting Y, Z, and W equal to zero, B_1 and B_2 have the values already given for pure Fe-Ni alloys. Considering the other constants one at a time, it is evident that their values are given by the slopes of the corresponding curves of Figs. 19 and 20. Evaluating these slopes:

$$C_1 = C_2 = -4.00$$
$$D_1 = D_2 = +\ 30$$
$$E_1 = E_2 = +\ 40$$

and substituting in equations 9a and 9b:

$$\alpha_1 \times 10^6 = 0.035\theta - 0.140Y + 1.05Z + 1.4W - 9.17 \qquad [10a]$$
$$\alpha_2 \times 10^6 = 0.035\theta - 0.140Y + 1.05Z + 1.4W - 8.12 \qquad [10b]$$

These equations apply to any composition with which θ falls between 350° and 500° to 600° C. and Ar$_3$ below atmospheric temperature.

Before accepting these equations, it is desirable to justify the remaining unconfirmed assumption on which they are based; namely, that the constant A of equation 7 is not changed by variation in composition. This may be done by substituting A for 0.035 in equations 10a and 10b, transposing and calculating its value from the observed expansion prop-

erty values of Table 2. The values obtained are given in Table 6. They come very close to the mean value 0.035 except for very low or high inflection temperatures, for which the equations do not apply. Such agreement would not exist if the value of A changed appreciably with the cobalt or manganese content. The effects of allowable carbon contents is insignificant, hence the original assumption is fully justified. The concordance of the calculated values of A also establishes the accuracy of the values used for this constant and for the other constants defining the effects of the composition variables.

TABLE 6.—*Values of Constants A_1 and A_2 Calculated from Observed Expansion Properties of Individual Alloys*

Alloy No.	$\theta°$ C.	A_1	A_2
1863	310	0.0349	0 0346
1864	325	345	347
1794	370	356	360
1912	420	350	346
1718	430	356	350
10	510	345	342
		Mean 0.0350	0 0349
1782	240	(0 0417)	(0 0435)
2031	295	383	378
1783	335	361	348
2034	375	347	346
1784	425	342	344
1987	450	347	348
1988	450	356	352
1989	495	346	349
		Mean 0 0355	0 0352
2125	400	0.0350	0 0349
2123	415	347	345
2091	460	349	350
2114	465	342	346
2092	480	348	350
2127	550	346	347
2118	620	340	345
		Mean 0 0346	0.0347

$$A_1 = \frac{\alpha_1 \times 10^6 + 0.14Y - 1.05Z - 1.4W + 9.17}{\theta}$$

$$A_2 = \frac{\alpha_2 \times 10^6 + 0.14Y - 1.05Z - 1.4W + 8.12}{\theta}$$

The equations thus established are useful in their present form, but the major object of this investigation is to find the optimum compositions. The attainment of this objective requires the determination of whether or not manganese or carbon can be added to advantage, a possibility

previously suggested. For this purpose it is necessary to introduce the composition limitation as to maximum permissible cobalt content expressed by equation 5. Introducing this restriction by elimination of the cobalt variable from equations 10a and 10b gives:

$$\alpha_1 \times 10^6 = 0.024\theta + 0.38Z - 1.2W - 6.65 \qquad [11a]$$
$$\alpha_2 \times 10^6 = 0.024\theta + 0.38Z - 1.2W - 5.60 \qquad [11b]$$

which are the equations desired. They hold when Ar_3 is depressed to approximately $-100°$ C.; i. e., for nickel and cobalt contents given by equations 5 and 6.

In order to apply the foregoing equations it is necessary to assign values to the inflection temperature and the manganese and carbon contents from consideration of the conditions of the particular problem at hand. For example, to find the expansion properties of alloys containing conventional contents of secondary elements and the maximum feasible cobalt content, substitute % Mn = 0.7 and % C = 0.1, in equations 11a and 11b, whence:

$$\alpha_1 \times 10^6 = 0.024\theta - 6.50$$
$$\alpha_2 \times 10^6 = 0.024\theta - 5.45$$
$$\% \ Ni = 37.4 - 0.0282\theta$$
$$\% \ Co = 0.0795\theta - 12.8$$

It remains only to introduce an appropriate value of the inflection temperature, θ, to find the expansivities obtainable therewith and the nickel and cobalt contents necessary to give these properties. The values obtained from these equations also furnish a check on the accuracy of the equations for they should give very closely the expansion properties of alloys 2091, 2092, 2125 and 2127, and in fact do so.

Looking at the final equations, 11a and 11b, from the viewpoint of the best attainable compositions, it may be seen from the signs of the respective terms that manganese is detrimental and carbon beneficial when the maximum feasible cobalt content is maintained. The benefit conferred by carbon is indirect because it lowers the merit index slightly when other elements are constant. The meritorious effect of carbon is due to the fact that it is extremely active in lowering Ar_3 and this permits correspondingly large additions of cobalt. The maximum advantage attainable with reversible expansivity, however, is small, about 0.4×10^{-6} per deg. C., because the maximum carbon content is restricted to about 0.3 per cent. The optimum expansivity is, therefore, obtained with 0.3 per cent. C and 0 per cent. Mn when the cobalt content has its maximum feasible value. Actually 0.2 per cent. Mn does little harm to the expansion properties although its metallurgical effect is such as to greatly facilitate commercial manufacture of these alloys. Consequently one may obtain the composition and expansivity of the best practicable alloys by

substituting % Mn = 0.2 and % C = 0.3 in equations 11a and 11b, from which:

$$\alpha_1 \times 10^6 = 0.024\theta - 6.9$$
$$\alpha_2 \times 10^6 = 0.024\theta - 5.9$$
$$\% \text{ Ni} = 35.6 - 0.282\theta$$
$$\% \text{ Co} = 0.0795\theta - 11.5$$

These equations have the same significance as the preceding, in which θ is the only independent variable.

The preceding discussion shows the desirability of keeping the manganese content down. It is not as important so far as expansivity is concerned in the alloys of maximum feasible cobalt content as in cobalt-free alloys. Comparison of the manganese terms of equations 10 and 11 shows that the harmful effect of manganese in alloys of maximum feasible cobalt content is less than 0.4 of that in cobalt-free alloys. There is another factor, however, which makes manganese highly undesirable in the high-cobalt alloys also; namely, the high cost of cobalt. Equation 5 shows that a cobalt increment nearly five times the manganese increment is necessary to maintain the desired composition property relations. Economy as well as expansivity requires, therefore, the minimum practicable manganese content in these alloys.

The equations given for expansivity apply only to alloys whose inflection temperatures are above 350° C. Alloys of lower expansivity, such as invar, are of considerable importance also, so it is of some interest to consider the improvements possible with them by the substitution of cobalt for nickel. Here the equations 1 to 6, which do not contain an expansivity term, hold also, though probably not so closely as for alloys having higher inflection temperature. Hence one may estimate the best compositions in this range also. A fair idea of the improvement in expansivity over that obtainable in the absence of cobalt may also be obtained by taking the difference between equations 10 with $Y = 0$ and equations 11. Denoting the difference in expansivity by $\Delta\alpha$:

$$\Delta\alpha \times 10^6 = 0.011\theta + 0.67Z + 2.6W - 2.52 \qquad [12]$$

for both minimum and mean expansivity. From this equation the improvement due to increasing the cobalt content to the maximum permissible point becomes greater as the manganese and carbon contents increase. On the basis of conventional values—0.5 per cent. Mn. and 0.1 per cent. C.— the improvement is given by:

$$\Delta\alpha \times 10^6 = 0.011\theta - 1.92$$

Taking the case of invar, $\theta = 225$° C. and the expansivity is lowered by 0.5×10^{-6} per deg. C. This is a substantial improvement over invar, which has a minimum expansivity of about 1.0×10^{-6} per deg. C. By taking advantage of this, a higher degree of dimensional stability in the

cold-worked condition may be attainable in the proposed alloy than is possible with invar.

SUMMARY

Mr. Brace's discovery that the addition of cobalt lowers the expansivity of low-expansion nickel-iron alloys suggested detailed investigation of the iron-nickel-cobalt system with the object of determining optimum compositions and their associated expansion properties. The results of such an investigation are described here.

Early in this work it was recognized that the improvement of the expansion properties attainable by the addition of cobalt is strictly limited by the gamma-alpha (Ar_3) transformation of iron. Consequently an initial series of alloys was prepared with cobalt variable and the nickel content constant and sufficiently high to depress Ar_3 below atmospheric temperatures. The expansion curves of these alloys show the same characteristics as do those of nickel steels; namely, a region of low expansivity followed by a sharp rise in expansivity with increasing temperature. In order to make possible numerical expression of the expansion characteristics of the various alloys, three values were taken from each curve and identified as "inflection temperature," "mean expansivity" and "minimum expansivity" respectively. The inflection temperature gives the upper limit to the temperature range of low expansivity, the mean expansivity gives expansion per unit length from 0° C. to the inflection temperature divided by that temperature, while the minimum expansivity gives the lowest value of the slope of the expansion curve.

Graphical coordination of the data on the preliminary series of alloys showed that:

1. The inflection temperature is unchanged by the substitution of cobalt for nickel.

2. The minimum, or mean, expansivity is lowered substantially in proportion to the amount of cobalt substituted for nickel.

Comparison of these alloys on the basis of equal inflection temperature led to the conclusion that the best expansion properties are to be obtained with the maximum substitution of cobalt for nickel, with which Ar_3 remains safely depressed below atmospheric temperatures. Ar_3 is considered to be safely depressed when at −100° C. So low a temperature is taken because small variations in manganese and carbon content from an intended composition have a large effect on Ar_3. Aiming at −100° C., variations of the magnitude normally encountered in commercial alloy preparation are not likely to bring Ar_3 within the range of atmospheric temperatures to which these alloys may be exposed in industrial applications such as thermostatic devices.

In accordance with the foregoing conclusion, it was sought to determine the range of composition of the Fe-Ni-Co alloys (containing nominal

amounts of manganese and carbon) within which Ar₃ is safely depressed. Both hardness and expansion tests were used to determine whether or not Ar₃ had occurred between atmospheric and liquid-air temperatures. These tests showed that Ar₃ is depressed to about $-100°$ C. when the ratio of the equivalent nickel content to the iron content of an alloy has the value of 0.55 irrespective of its cobalt content up to 50 per cent. at least. The equivalent nickel content is defined by:

$$\% \, L = \% \, \text{Ni} + 2.5(\% \, \text{Mn}) + 18(\% \, \text{C})$$

when the manganese content is below approximately 5 per cent. and the carbon content less than 0.3 per cent. This condition allows the maximum permissible cobalt content to be expressed in terms of the other components normally determined analytically, thus:

$$\% \, \text{Co} = 1.55(\% \, \text{Ni} + \% \, \text{Co}) + 3.05(\% \, \text{Mn}) + 18.5(\% \, \text{C}) - 55 \quad [2]$$

This simple relation was established after it was discovered that the lowering of Ar₃ by a given increase in the ratio of the nickel to the iron content is substantially the same in the presence of cobalt as in its absence.

In the light of the foregoing information alloys of intermediate and maximum permissible cobalt contents were prepared and tested. Graphical representation of the data obtained permitted the conclusion that the merit of an alloy may be expressed by a single value obtained by subtracting the expansivity divided by 0.035×10^{-6} from the inflection temperature. This "merit index" was found to vary linearly with the weight percentage of the individual components in such a way as to justify the conclusion that the effects of cobalt and manganese on the expansion properties are additive and that that of carbon is negligible.

These observations suggested the possibility of expressing the test results in the compact form of equations and furnished the values of the necessary constants. Writing θ for inflection temperature, X for the nickel content, Y for the cobalt content, Z for the manganese content and W for carbon content, the inflection temperature of any alloy of the group studied is given by:

$$\theta = 19.5(X + Y) - 22Z - OW - 465 \quad [4]$$

Introducing the restriction as to Ar₃, equation 2, the cobalt and nickel contents with which Ar₃ remains depressed to about $-100°$ C. are given by:

$$Y = 0.0795\theta + 4.8Z + 19W - 18.1 \quad [5]$$
$$X = 41.9 - 0.0282\theta - 3.7Z - 19W \quad [6]$$

when the inflection temperature comes between $200°$ and $600°$ C. The expansivities obtainable with these compositions are given by:

$$\alpha_1 \times 10^6 = 0.024\theta + 0.38Z - 1.2W - 6.65 \quad [11a]$$
$$\alpha_2 \times 10^6 = 0.024\theta + 0.38Z - 1.2W - 5.6 \quad [11b]$$

where α_1 is the minimum expansivity and α_2 is the mean expansivity when θ comes between 350° and 600° C.

The equations for expansivity show that manganese is detrimental in the low-expansion alloys containing the maximum permissible cobalt contents and that carbon is beneficial. Consequently the optimum compositions are those required by equations 5 and 6 when the manganese content is zero and the carbon content has its highest permissible value, about 0.3 per cent. The favorable effect of carbon is indirect, for the reason that its effect upon Ar_3 is such as to permit the use of higher cobalt contents than would otherwise be allowable with regard to the restrictions already set up. Manganese, on the other hand, is not only directly harmful, but is also undesirable from an economic standpoint because its presence requires a compensating addition of cobalt approximately five times as great.

The expansivity equations do not hold for low inflection temperatures such as are required for minimum expansivity at atmospheric temperature. The beneficial effect of the substitution of cobalt for nickel may nevertheless be estimated approximately. In the case of invar, the expansivity in the ordinary temperature range can be reduced by about 0.5×10^6 per deg. C. This improvement in the expansivity of invar may make it possible to secure better dimensional stability than has been available hitherto.

ACKNOWLEDGMENTS

DISCUSSION

C. G. FINK, New York, N. Y. (written discussion).—The low-expansion Fe-Ni-Co alloys undoubtedly will be of increasing scientific and commercial value, and the data submitted by Mr. Scott are most valuable for further research in the field. We have for a number of years studied the expansion properties of the Fe-Ni and the Fe-Ni-Cu series. The copper-clad leading-in wire is a direct result of this study. This wire has a low-expansion Ni-Fe core with a copper sheath around it. Mr. Scott may be interested in the curve published on page 271 of volume 56 of the *Transactions* of the American Electrochemical Society, showing the coefficient of expansion of Fe-Ni alloys between 25° and 400°C., the coefficient of platinum being taken as 100.° It will be noted that invar has a coefficient of expansion almost as high as platinum within that temperature range.

H. SCOTT.—Professor Fink's remarks inspire a desire to hear further from him on the subject of copper-clad wire for sealing into glass, a subject which has received no attention in the literature commensurate with its industrial importance.

Metallography of Commercial Thorium

By Edmund S. Davenport,* Bloomfield, N. J.

THE production of thorium of high purity by the Ca-CaCl$_2$ reduction has been described by Marden and Rentschler,[1] who also reported some of the properties of the coherent, ductile metal obtained from this pure thorium powder.

The present paper describes the properties of thorium produced by the Ca-CaCl$_2$ process modified in some details to meet commercial conditions. The principal effect of these changes in process has been an unavoidable increase in the oxide content of the thorium.

MATERIALS AND METHODS

The thorium employed in this investigation was made from pure thorium oxide (ThO$_2$) by the Ca-CaCl$_2$ reduction. The washed and dried metal powder was pressed into bars approximately 0.160 in. dia. and 10 in. long, at a pressure of 75,000 lb. per sq. in. The bars were heat-treated in vacuum at 1175° C. for 1 hr. This treatment yielded ingots sufficiently dense and coherent for mechanical working. Thorium has been successfully worked without a protective metallic covering, but for the purposes of this investigation it was more convenient to inclose the ingots in soft iron tubes and swage or roll cold to the desired sizes. The iron sheath was dissolved with nitric acid, leaving the cold-worked thorium exposed.

CHEMICAL ANALYSES

Analyses of typical samples of the material used in this work are given in Table 1.

Thorium powder oxidizes in moist air, even at room temperature; no unusual precautions were taken to prevent such oxidation of the material used in this investigation. A certain amount of oxidation probably takes place during pressing; certainly during heat-treating unless a very slow heating schedule is employed. These factors account

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TABLE 1.—*Analyses of Thorium Samples*

	1 Treated Ingot, Per Cent.	2 0.003-in. Rolled Strip, Per Cent.	3 0.055-in. Swaged Rod, Per Cent.	4 Powder (in Vac.), Per Cent.
Sulfur	0 05	0.04		0.007
Silicon	0.03	0 03		0.009
Iron.	0.06	0 04		0.03
ThO₂, by difference	3.49	3.63		0.156
ThO₂, by planimetric count (microscope)....	3 65		2.86	
Thorium.				99.75

for much of the oxide appearing in Table 1. A slow and gradual heat treatment under the best conditions of vacuum will yield ingots of much lower oxide content than that shown in column 1, Table 1. Such special heat-treating conditions were not employed in the present work; the heat-treating of thorium has been discussed in detail by Marden and Rentschler.[2] The analyses in Table 1 probably represent the average purity that can be expected from large-scale operations at this time. An oxide content of 3 to 4 per cent., if uniformly distributed as small inclusions, does not impair the working properties of the metal. The powders as originally produced have a low oxide content, as demonstrated by column 4, Table 1, showing the composition of a powder sample that was kept sealed in vacuum until the analysis was commenced.

Exacting process conditions and technique will produce metal of low oxide content. However, for the present investigation it was thought advisable to select a material which might be termed commercial.

PROPERTIES INVESTIGATED

The effect of cold working on the following properties was determined: (1) specific gravity at 20° and 25° C.; (2) Rockwell B-scale hardness; (3) tensile properties; (4) annealing-temperature range; (5) microstructure, unetched and etched.

1. Specific Gravity

Results of specific gravity determinations by two independent observers are shown in Table 2 and Fig. 1. The specimens, suitably cleaned, were weighed in air and then in water at the temperature indicated. The specific gravities calculated from these data are referred to water at 4° C.

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[2] J. W. Marden and H. C. Rentschler: *Loc. cit.*

TABLE 2.—*Specific Gravity of Cold-worked Thorium*

Diameter, Inches	Reduction in Cross-section by Working, Per Cent.	Sp. Gr. at 20° C. Observer No. 1	Sp. Gr. at 25° C. Observer No. 2
Treated ingot	Unworked	10.50	10.23
0.150	13.2	11.09	11 04
0.100	61.7	11.36	
0.090	69.1	11.43	11.45
0.055	88.3	11.42	11.47
0 055[a]	88.3[a]		11.63[a]
0.003[a] strip	90.3[a]		11.29[a]

[a] Annealed.

The first cold-working operations brought about a pronounced increase in specific gravity which was followed by a more gradual approach to a constant maximum value. Thorium is similar, in this
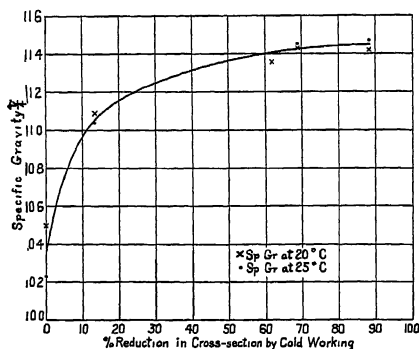
FIG. 1.—RESULTS OF DETERMINATIONS OF SPECIFIC GRAVITY BY TWO INDEPENDENT OBSERVERS.
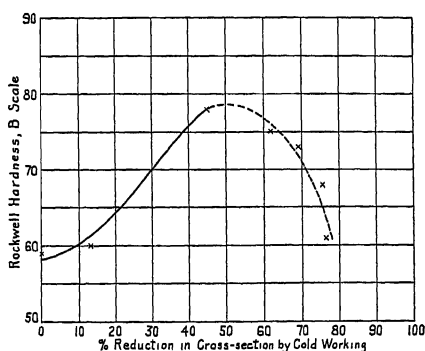
FIG. 2.—ROCKWELL HARDNESS DETERMINATIONS.

respect, to many other metals fabricated from the pressed and heat-treated powders.

2. *Rockwell Hardness*

Results of a large number of Rockwell B-scale hardness determinations are shown in Table 3 and Fig. 2. All determinations were made on polished longitudinal sections of the rods.

Hardness increased with cold working up to about 50 per cent. reduction in cross-section, after which an apparent softening took place with further working. This anomalous behavior is at variance with other data accumulated in this investigation on the effect of cold working and probably was caused by the splitting of severely worked rods under the Rockwell test load. Such splitting would result in low Rockwell values.

TABLE 3.—*Rockwell Hardness of Cold-worked Thorium*

Diameter, Inches	Reduction in Cross-section by Working, Per Cent.	Rockwell Hardness, Average	Number of Tests Averaged
Treated ingot	Unworked	B 59	20
0.150	13.2	B 60	110
0 120	44.6	B 78	90
0.100	61.7	B 75	30
0.090	69.1	B 73	120
0.080	75.5	B 68	10
0.075	76.4	B 61	20

3. Tensile Properties

Results of tensile tests on cold-worked rods and wire are given in Table 4 and Fig. 3.

TABLE 4.—*Tensile Properties of Cold-worked Thorium*

Diameter, Inches	Reduction in Cross-section by Working, Per Cent.	Tensile Strength (Lb per Sq.In.)	Avg.	Elongation in 1 In., Per Cent.	Avg.
Treated ingot	Unworked	38,600		6.0	
		37,900		3.5	
		36,300		3.0	
		40,800	38,400	5.5	4.5
0.149	14.7	39,600		1.5	
		44,700	42,150	3.0	2.3
0.092	67.7	62,200		2.0	
		50,400	56,300	1.0	1.5
0.088	70.1	71,300		1.0	
		80,600		1.5	
		77,500	76,500	2.0	1.5
0.054	88.7	87,400		0.5	
		87,400		0.0	
		83,000	85,900	1.0	0.5

In common with most metals, the tensile strength of thorium increases and percentage elongation decreases with cold working. There was no appreciable reduction in area at point of fracture.

4. Annealing-temperature Range

Annealing-temperature ranges were determined on material of the three following degrees of cold work:

13.2 per cent. reduction by working (0.150-in. rod),
44.7 per cent. reduction by working (0.120-in. rod),
69.1 per cent. reduction by working (0.090-in. rod).

Annealing was carried out in vacuum, except where otherwise noted, and at temperatures from 100° to 1230° C. All specimens were held for 30 min. at the indicated temperature and cooled in vacuum in the furnace. Rockwell B-scale hardness was used to measure the degree of annealing obtained. The results are given in Table 5. In Fig. 4 the ratio $\frac{H}{A}$ or $\frac{\text{Cold-worked Hardness}}{\text{Annealed Hardness}}$ is plotted against annealing temperatures. Expressing the results in the form of such a ratio eliminates irregularities caused by slight hardness differences among the cold-
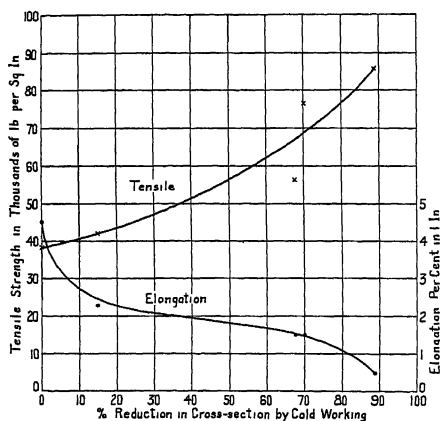
FIG. 3.—RESULTS OF TENSILE TESTS ON COLD-WORKED RODS AND WIRE.
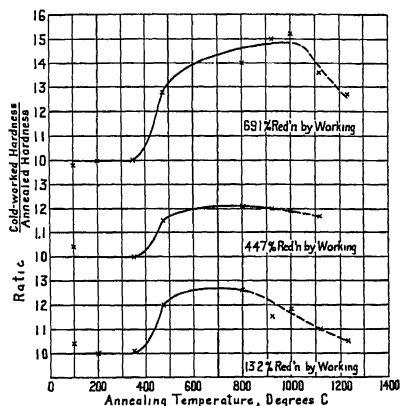
FIG. 4.—RATIO H/A PLOTTED AGAINST ANNEALING TEMPERATURES.

worked specimens of any one group. The specimens of Table 5 and Fig. 4 were not reground or resurfaced after annealing; i. e., they were tested just as removed from the furnace. Table 6 shows hardness data obtained on these same specimens after removal of the surface layers after annealing. These data are not reproduced graphically, because they show the same general features as the curves of Fig. 4, although in a more pronounced manner.

Annealing begins to take place for all three degrees of cold work between 300° and 400° C., and maximum softening is reached in the range of 800° to 1000° C. At temperatures above 900° to 1000° C. a hardening effect was observed. This appears in the curves of Fig. 4 as a decrease in the ratio H/A at the higher temperatures. This hardening was probably due to carbonaceous or other gaseous impurities in the vacuum furnace at the time of annealing. Such impurities would combine readily with thorium, which is very active at high temperatures.

TABLE 5.—*Rockwell Hardness of Annealed Thorium*

Annealing Temperature, Deg. C.	13.2 Per Cent. Reduction (0.150 in.)			44 7 Per Cent. Reduction (0.120 in.)			69.1 Per Cent. Reduction (0.090 in.)		
	Before Anneal-ing (H)	After Anneal-ing (A)	Ratio $\frac{H}{A}$	Before Anneal-ing (H)	After Anneal-ing (A)	Ratio $\frac{H}{A}$	Before Anneal-ing (H)	After Anneal-ing (A)	Ratio $\frac{H}{A}$
100[a]	B 52	B 50	1.04	B 79	B 76	1 04	B 75	B 77	0 98
200[a]	67	67	1 00				75	75	1.00
350	66	65	1.01	59	59	1 00	73	73	1.00
475	55	46	1 20	78	68	1.15	74	58	1.28
800	63	50	1 26	76	63	1.21	73	52	1.40
920	53	46	1.15	78	65	1.20	75	50	1.50
1000	54	46	1.18	80	67	1.19	64	42	1.52
1115	64	58	1 10	81	69	1.17	72	53	1.36
1230	68	65	1 05				71	56	1 27
	B 60 Avg.			B 76 Avg.			B 72 Avg.		

[a] Annealed in air

TABLE 6.—*Rockwell Hardness of Annealed and Resurfaced Thorium*

Annealing Temperature, Deg. C.	13.2 Per Cent. Reduction (0 150 In.)			44.7 Per Cent. Reduction (0.120 In.)			69.1 Per Cent. Reduction (0 090 In.)		
	Before Anneal-ing (H)	After Anneal-ing (A')	Ratio H/A'	Before Anneal-ing (H)	After Anneal-ing (A')	Ratio H/A'	Before Anneal-ing (H)	After Anneal-ing (A')	Ratio H/A'
350	B 66	B 57	1.16	B 59	B 58	1 02	B 76	B 74	1.03
475	55	35	1.57	78	66	1.18	74	55	1.35
800	63	37	1 70	76	55	1 38	73	37	1 97
920	53	34	1.56	78	57	1 37	75	38	1.97
1000	54	37	1.46	80	60	1.33	64	41	1 56
1115	64	43	1.49	81	60	1.35	72	42	1 71
1230	68	54	1.26				71	40	1.78

There was considerable evidence to support this explanation, although the experiment is to be repeated under better conditions of vacuum. It was observed that annealing at 350° C. in air caused a small but definite hardening effect, whereas annealing at the same temperature in vacuum produced no change in hardness. These facts demonstrate the importance of control of furnace atmosphere in the annealing of thorium.

5. *Microstructure*

Specimens of thorium may be prepared for microscopic examination by ordinary metallographic methods, care being taken to avoid over-heating in grinding and polishing. The polished surface tarnishes gradually in the atmosphere and photographs should be taken on freshly

prepared specimens. For visual work, however, the specimens retain a satisfactory surface for several weeks after the completion of polishing.

Figs. 5 and 6 show unetched specimens of thorium. Fig. 5 represents one of the treated, unworked ingots. The small dark spots are inclusions of thorium oxide (ThO_2); these have a characteristic, blue-gray color when viewed under the microscope; the larger black areas are voids. Fig. 6 shows the effect of cold working on the unetched structure. The voids are closed by the working and the oxide particles aligned parallel to the axis of the rods.

Considerable experimentation was carried out before a suitable etching technique for thorium was developed. Most of the reagents that attack thorium also oxidize it so readily that structural features
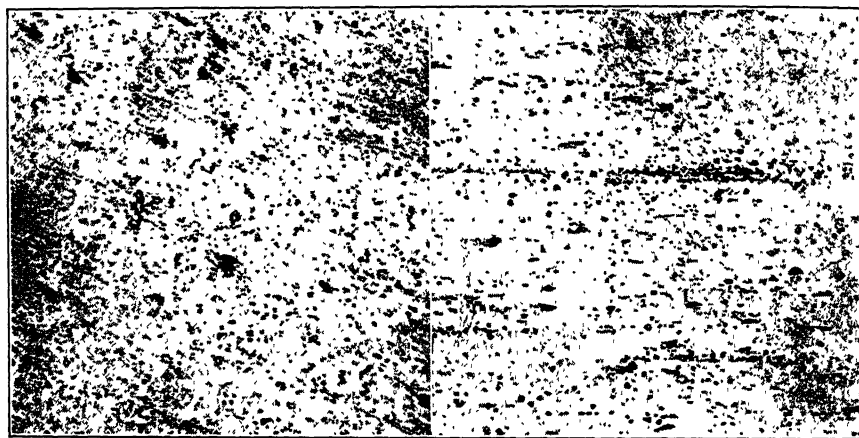
FIG. 5.—TREATED INGOT. × 200. UNETCHED.

FIG. 6.—SWAGED ROD, 0.055-IN. 88.3 PER CENT. REDUCTION. × 200. UNETCHED.

are obscured. The best results have been obtained by electrolytic etching, employing a 10 per cent. solution of nitric acid in glacial acetic acid. The specimen is made the anode and a current of $\frac{1}{4}$ to $\frac{1}{2}$ amp. is used for 30 sec. or longer, depending on the depth of etch required. A powdery, black deposit forms on the specimen, which may be rubbed off with the finger or a soft cloth during rinsing in alcohol. This etching treatment leaves the specimen covered with an extremely thin, iridescent film of oxide which tends to obscure fine structural details at low magnification, although general features may be discerned. These thin oxide films are almost invisible when using oil-immersion objectives. Figs. 7 to 11 inclusive show etched structures taken with a 2-mm. oil-immersion objective. Fig. 7 represents one of the treated, unworked ingots. Voids and oxide particles have been rendered conspicuous by etching and it is difficult to distinguish between them except by actual observa-

FIG. 7.—TREATED INGOT.

FIG. 8.—SWAGED ROD, 0.150-IN. 13.2 PER CENT. REDUCTION.

FIG. 9.—SWAGED ROD, 0.100-IN. 61.7 PER CENT. REDUCTION.

FIG. 10.—SWAGED ROD, 0.080-IN. 75.5 PER CENT. REDUCTION.

FIG. 11.—SWAGED ROD, 0.055-IN. 88.3 PER CENT. REDUCTION.

ALL × 1000; ETCHED ELECTRO-LYTICALLY.

tion under the microscope.   Many of the voids are in the grain boundaries and are undoubtedly of the same nature as the intergranular pits[3] observed in recrystallized tungsten, molybdenum and other metals fabricated from the pressed powders.   The progress of cold working
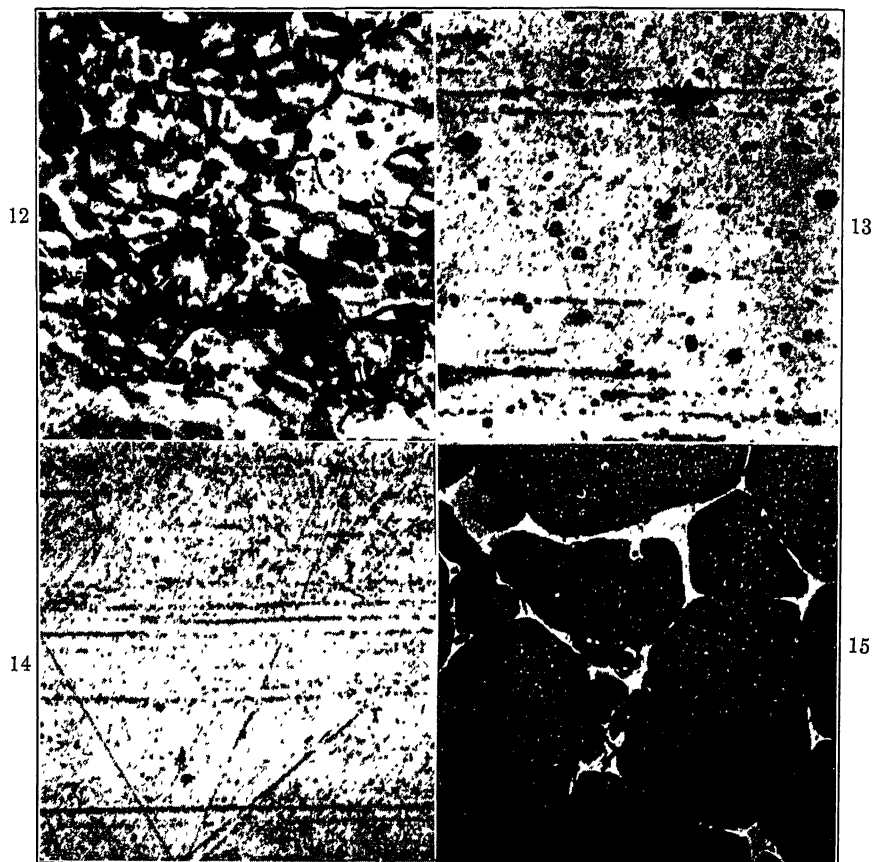
FIG. 12.—ANNEALED ROD, 0.055-IN.   × 1000.   ETCHED ELECTROLYTICALLY.
FIG. 13.—WIRE (0.029-IN.) WITH LARGE ThO₂ INCLUSIONS.   × 300.   UNETCHED.
FIG. 14.—WIRE (0.029-IN.) WITH SMALL ThO₂ INCLUSIONS.   × 300.   UNETCHED.
   FIG. 15.—INTERGRANULAR CONSTITUENT IN IMPURE THORIUM.   × 500.   ETCHED
WITH BOILING ALKALINE SODIUM PICRATE.

is shown in Figs. 8 to 11 inclusive.   At 0.055-in. dia., the smallest size included in this investigation, the grains are severely deformed and are approaching the fibrous condition.

In Fig. 12 is shown the etched structure of 0.055-in. wire after annealing for 1 hr. at 900° C.   The axis of working is indicated by the alignment

[3] E. S. Davenport: Grain Boundary Phenomena in Tungsten Filaments. *Proc.* Inst. Metals Div., A. I. M. E. (1927) 413.

of the ThO_2 inclusions, although the grain structure has been completely equiaxed by the annealing treatment.

Discussion of Results

The foregoing properties of commercial thorium represent a given set of pressing and heat-treating conditions of the powder. Certain properties, particularly density, hardness and tensile strength of the treated ingots, may be expected to vary somewhat, depending on these pressing and treating conditions.

It is interesting to note that thorium wire in the fibrous condition, represented in Fig. 11, may be bent and coiled at room temperature, although the ductility as measured by the tensile test is very low. In this respect thorium resembles tungsten, molybdenum and other metals that exhibit ductility in the fibrous condition.

MICROSTRUCTURAL IMPURITIES

Brief reference has been made to thorium oxide (ThO_2) inclusions. The size, shape and distribution of the oxide particles may vary widely, depending on the previous history of the specimen. Figs. 13 and 14,
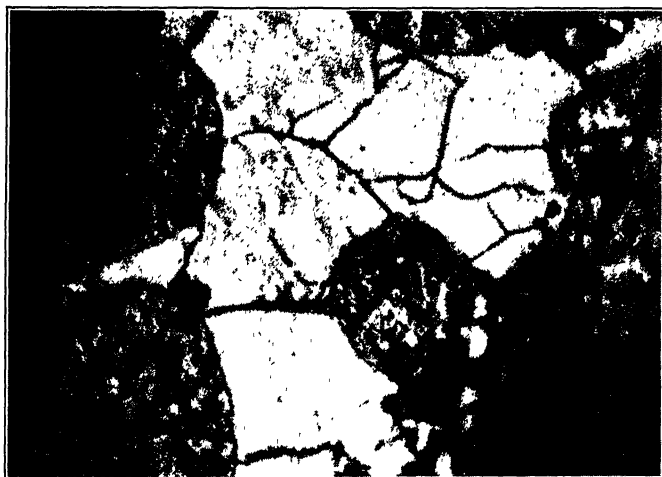
FIG. 16.—INTERGRANULAR IMPURITY SHATTERED BY COLD WORKING. × 2000.
ETCHED WITH BOILING SODIUM PICRATE.

both of unetched 0.029-in. wire, show two types of oxide distribution. In Fig. 13 the particles are fairly large and many are distinctly angular in shape. Large oxide inclusions of this type may cause splitting on severe cold working. In Fig. 14 the oxide particles are extremely small, in fact, hardly resolvable at the magnification employed; this type of oxide distribution is less harmful to working properties.

A constituent which has been identified with the presence of carbon in thorium is shown in Figs. 15 to 18 inclusive. It is a hard, white constituent, frequently located in the grain boundaries, as shown in Fig. 15; it will be referred to as "carbide" in the following discussion,

FIG. 17.—INTERGRANULAR IMPURITIES IN CAST THORIUM.   × 200.
FIG. 18.—SAME AS FIG. 17.   × 1000.
BOTH SPECIMENS "AIR-ETCHED."

although exact information as to its constitution is lacking at this time. The brittle nature of this constituent is illustrated in Fig. 16, which shows thorium that broke up with a small amount of cold working. Mechanical working shattered the hard, brittle constituent, as shown by numerous cracks in the area photographed. These large carbide

areas show a secondary phase, suggesting the probable existence of more than one constituent. The specimens of Figs. 15 and 16 were etched in boiling, alkaline sodium picrate, which darkens the thorium matrix and brings the carbide out in brilliant contrast. Any appreciable amount of these carbide impurities is detrimental to the working qualities of thorium.

Fig. 17 shows the structure of thorium melted in vacuum in which there were traces of carbonaceous vapors and probably other gases. The carbide constituent is seen to form a eutectic under these conditions. This specimen was "air-etched"—that is, allowed to tarnish in air—which gradually darkens the thorium matrix. An area of the same specimen is shown in Fig. 18 at higher magnification. Four constituents may be seen in this micrograph: (1) the dark, thorium background; (2) the white eutectic formations; (3) angular and dendritic inclusions of blue-gray oxide; (4) needles or plates of an orange-colored constituent which occasionally appear to be transparent; this last constituent has not yet been identified.

SUMMARY

The properties of commercial thorium made by the Ca-CaCl₂ process have been determined, with particular reference to the effect of cold work. Specific gravity, hardness, tensile strength and ductility, annealing temperature and microstructure were investigated. A method of etching thorium for microscopic examination has been described and certain impurities have been illustrated and discussed.

DISCUSSION

M. M. AUSTIN, N. Chicago, Ill.—I have been impressed by the similarity in appearance of thorium carbide as shown in Figs. 15 and 17 with structures which we have definitely identified as tantalum silicide. Our own observations have been made on samples of pure tantalum to which silicon was intentionally added. The "jellyfish structure" of Fig. 15, also the strung-out structure and eutectic of Fig. 17 are practically identical in appearance with photographs we have made of tantalum silicide.

I realize that it is not safe to go very far in drawing conclusions from their appearance as to the probable nature of metallographic constituents. However, in this

case I believe it would be well to consider the possibility that these inclusions may be thorium silicide.

E. S. DAVENPORT.—The point is a good one. I do not feel that the identification of this compound, which we have provisionally termed "carbide," is entirely established. We have thought that possibly it might be a silicide, or a compound with one of the metallic elements such as iron. We have considerable evidence however which points to its being a compound with carbon. Whenever we find a large amount of this constituent in the metal we always get pronounced hydrocarbon odors from the specimen, and other evidence confirms this. The proper identification of this constituent awaits better methods of chemical analysis, which have not been completely worked out as yet.

C. E. PLUMMER, Chicago, Ill.—Several years ago a sample of thorium metal was submitted to me for the determination of the oxygen content. An effort was made to apply the Jordan and Eckman vacuum fusion method for the determination of oxygen in thorium metal. I am rather interested to know whether the oxygen content of this metal was known, or whether any work has been done to estimate the amount of oxygen in the metal made by this process. The method that we tried for the determination of oxygen in thorium metal was a rather novel one, and the results obtained at that time were indicative that the following method had possibilities.

We took iron, melted it *in vacuo* in the presence of iron sulfide, and then removed the rich iron sulfide layer on top, so we had a product that was saturated with sulfur and carbon. We remelted that product *in vacuo* until we no longer had gases coming off. Then we took a known amount of thoria and thorium and mixed them with this iron saturated with carbon and sulfur. Applying the Jordan-Eckman method, we obtained almost theoretical amounts of oxygen as added in the form of thorium oxide. We worked upon the theory that the thorium had a greater affinity for sulfur than it did for oxygen, and therefore the thorium would go over to sulfide and leave the oxygen in condition to be collected as carbon monoxide, or carbon dioxide. We were able to recover 95 per cent. of the oxygen as added in the form of thorium oxide.

Although this work never was completed, this method was turned over to Dr. Eckman and Mr. Jordan, of the U. S. Bureau of Standards, for further investigation

I suggest that perhaps this is a possible method for determining oxygen in thorium metal.

E. S. DAVENPORT.—I am not enough of an analyst to comment on Mr. Plummer's discussion, except to say that any improvement in the analytical methods for these rarer metals will be a step in advance. All I can say about these oxide determinations is that the oxide was determined in a manner similar, I believe, to the way in which thorium oxide is determined in thoriated tungsten; that is, by burning a sample of the metal and calculating the difference in weights before and after burning.

All of the analytical methods for these metals are open to considerable improvement.

S. L. HOYT, Schenectady, N. Y.—The author stated that the high-temperature sintering or treating of thorium causes the oxide particles to increase in size. Do they also decrease in number? What I have in mind is, is there any oxidation or diffusion in thorium at the high temperature observed?

E. S. DAVENPORT.—The oxide particles apparently do decrease in number as they increase in size. Comparison between Figs. 13 and 14 shows that. Although these two samples were not originally from the same batch of metal, the general comparison holds true. In all of the cases that we have observed, where the oxide particles are very large, they are fewer in number, and where they are very small, as in Fig. 14, there will be a larger number of them.

Working Properties of Tantalum

By M. M. Austin,* Chicago, Ill.

Pure metallic tantalum, from a practical standpoint, is one of the newer developments in the metal field. Although it was used as filament in incandescent lamps in 1906, only within the last five years has the metal been available in sufficient quantity and suitable form for more general application. In addition to corrosion-resisting properties and high melting point, the metal has an ability to withstand unusual amounts of cold working. It affords some striking demonstrations of block movement during plastic flow.

Strength and Ductility of Tantalum

Since there is no good way of defining working properties numerically, illustrations will be used. It is possible to roll a bar of pure tantalum 0.4 in. thick to sheet 0.001 in. thick, without heating or annealing. The sheet produced will be sound and may be bent upon itself at right angles to the direction of rolling. Longitudinally the sheet will be somewhat brittle. A disk of annealed metal may be cupped and drawn to the form of a capsule $\frac{3}{16}$ in. dia. by $1\frac{1}{8}$ in. long. If carefully handled this capsule can be further deformed by drawing to a tube having an outside diameter of 0.050 in. Disks of tantalum may be spun into tubes of $\frac{1}{2}$ in. dia. and $1\frac{1}{2}$ in. long. In the form of rod, reductions may be made from 0.4 in. to 0.001 dia. In the latter process, it is necessary to heat the wire four or five times to 500° C., at intervals between 0.040 and 0.001 in. Although the melting point of tantalum is 2850° C., these heatings at 500° C. are sufficient to distinctly anneal it.

Published figures on the strength and ductility of tantalum are not particularly accurate. This is due to the fact that these properties vary widely, depending on the extent to which the metal is contaminated by gas. There are no sharp critical points in these changes with gas content; samples of metal will vary from a springy or actually brittle condition to one of leadlike softness. Samples that have had a prolonged heating at high temperatures in a good vacuum, under conditions such as would be provided in vacuum-tube experimentation, will yield a product of about the hardness of annealed copper. The usual commercial metal will have the hardness of annealed mild steel.

* Metallurgist, The Fansteel Products Co. Inc.

Although metal that has been cold-worked as described will not be excessively hard or brittle, it will be entirely lacking in drawing qualities, except as wire, and will show no elongation in tension. Thorough annealing of the metal to a substantially equiaxed condition requires heating for a short period at 800° to 1000° C. Annealed material will show an elongation of 30 per cent. in 10 in. Since the metal oxidizes and absorbs gases rapidly above a red heat, it is necessary to conduct annealing operations in a good vacuum. Metal that has been severely cold-worked in one direction shows but slight directional properties after it has been annealed. What directional properties do exist are due to orientation of grains into preferred positions, as is shown by the fact that a cup drawn from a disk exhibits the characteristic four-sided scallop. In view of the necessity for vacuum annealing, it is particularly fortunate from a practical standpoint that the metal may be worked under such adverse conditions.

EXPLANATION OF PROPERTIES OF TANTALUM

The information available to explain these unusual properties of tantalum is incomplete, and, in places, contradictory. Such X-ray studies as have been made place the metal in the body-centered cubic group along with the alkali metals and with vanadium, chromium, iron, molybdenum and tungsten. From a theoretical standpoint, this group should be less ductile than the face-centered group, because of the smaller facility for slip which the particular arrangement of atomic planes provides. Molybdenum and tungsten exhibit great ductility when handled in a special way, but it is not easy to draw analogies. The metals are dense, have high melting points and are closely grouped in the periodic system. However, tantalum is soft and does not show intercrystalline brittleness, while molybdenum and tungsten are hard and remarkably stiff even at elevated temperatures and show marked intercrystalline brittleness at room temperature. It is possible that an X-ray study of the nearly pure and gas-free metal now available might help to clear up these discrepancies.

It seems probable that the high-temperature high-vacuum treatment to which tantalum is subjected in process of manufacture may have something to do with its plasticity. This treatment not only removes the gases to which the metal is particularly susceptible, but must also reduce to a small concentration other impurities of which the vapor pressures would be high at these temperatures.

BLOCK MOVEMENT AND SLIP

From the characteristics described, tantalum might be expected to display unusual evidence of a capacity for block movement and slip.

A series of photographs is presented in this connection.   When tantalum that has been considerably cold-worked is heated to a high degree, say to within 100° or 200° C. of its melting point, it is prone to form large crystalline grains, which occupy the whole thickness of the rod or sheet. When rods of this sort are pulled, block movements occur, which are visible to the unaided eye.   When a failure occurs, the characteristic
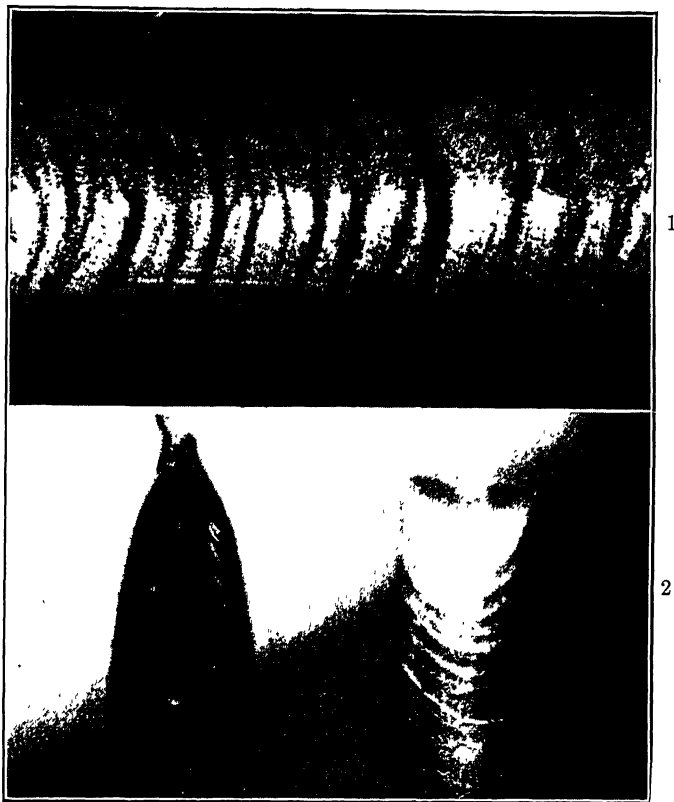
FIG. 1.—SINGLE-CRYSTAL TANTALUM ROD 0.1 IN. DIA., SHOWING LARGE BLOCK MOVEMENTS RESULTING FROM STRAIN.

FIG. 2.—SIDE AND EDGE VIEW OF WEDGE-SHAPED FRACTURE IN SINGLE-CRYSTAL TANTALUM ROD OF 0.1 IN. DIA., SHOWING BLOCK MOVEMENTS WHICH FORMED THE WEDGE.

wedge-shaped form of a single-crystal fracture develops and the block movements that have produced it are plainly evident.   The magnitude of the block movements depends on the dimensions of the unit and in a fine wire the microscope is required to see these movements.   Figs. 1, 2 and 3 show specimens of this sort.   When sheet containing such large crystals is slightly rolled, the grain boundaries may be seen plainly and the contours of the free edges afford striking evidence of the varying resistance of

different grains to the force applied. There is also evidence of greater hardness at the grain boundaries and of a marked side thrust where the orientation is such as to permit the grains to flow more easily at right angles than parallel to the direction of rolling. This behavior is shown in Figs. 5 and 6.

A demonstration of block movement of this sort naturally leads to an examination of some of the theories that have been presented to
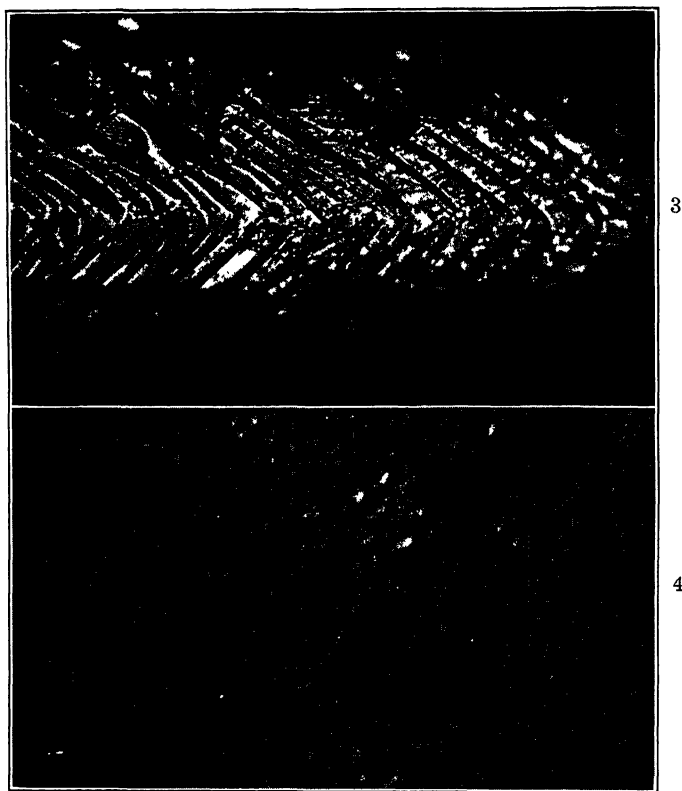
FIG. 3.—TANTALUM WIRE 0.005 IN. DIA., SHOWING MINUTE BLOCK MOVEMENTS DUE TO STRAIN.   × 500.

FIG. 4.—SLIP BANDS IN FINE-GRAINED TANTALUM.   × 2000.

explain them. The principal concern has been over the reasons for the occurrence of slip over a very small proportion of the available slip surfaces and the reason for their stopping. Fig. 4 shows the appearance of the slip planes produced on the polished surface of a fine-grained specimen. Compared with Figs. 1 and 2, these planes are infinitely more closely spaced. The principal difference between these specimens is in the size of the unit to which force is being applied and the rate of change

in the direction of the forces as deformation proceeds.   From this it would seem that these factors are important in determining what slip bands will occur.   Tantalum can hardly be regarded as a special case so far as mechanism of flow is concerned and it follows, therefore, from the tremendous amount of plastic deformation which the metal will stand, that a much larger proportion of the potential slip planes may come into action than is usually supposed possible.   If the formation of slip planes
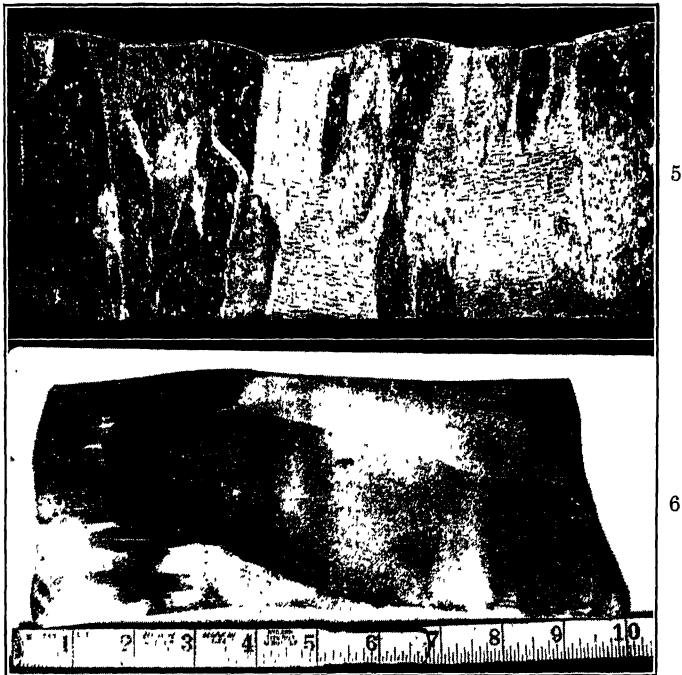
FIG. 5.—SPECIMEN OF TANTALUM.   ABOUT NATURAL SIZE.
Upper edge shows varying hardness of different grains depending on orientation, also greater hardness at grain boundaries.   Sheet has been slightly rolled since grains were formed, and etched to give more contrast.

FIG. 6.—COARSE-GRAINED TANTALUM SHEET, LIGHTLY ROLLED AND ETCHED.   THE PIECE WAS RECTANGULAR BEFORE ROLLING.

proceeds continuously with increasing amounts of cold work, all of the atomic layers may be brought into action providing the proper force is brought to bear upon them.   It must be remembered, however, that as deformation proceeds on a given set of planes under force from a given direction, the planes change position in a way to resist the force more strongly.   As force is increased and deformation continues, new systems of planes will come into action, but blocks of undisturbed metal of large atomic dimension might remain even after large amounts of working.

CONCLUSION

The author does not want to give the impression that the working of tantalum under the extreme conditions described is either necessary or desirable; nor does he attach any practical importance to the behavior of the coarse-grained metal. Ordinarily an effort is made to produce a fine-grained metal and to work it under the most favorable conditions. The facts and figures seem unusual, and have been given in the hope that they may stimulate discussion and possibly round out the ideas of others regarding the plasticity of metals.

Determining Orientation of Crystals in Rolled Metal from X-ray Patterns Taken by Monochromatic Pinhole Method

By Wheeler P. Davey,* State College, Pa., C. C. Nitchie† and M. L. Fuller,† Palmerton, Pa.

When metals are subjected to mechanical working, such as rolling, one of the phenomena that take place is a movement of the crystals of the metal into a system or systems of orientation which bear an angular relation to the direction of working. In rolled metal the crystals may orient themselves with respect to the rolling plane or the rolling direction, or both.

Direct evidence of the existence of preferred orientations in rolled metal has been obtained by numerous investigators from X-ray patterns of the rolled metal. Most of these workers used a monochromatic pinhole method.

Where the degree of preference for a single orientation is high the monochromatic pinhole pattern may be interpreted by a geometrical calculation based on the angular relationships of the planes in the crystal and the diffraction arcs on the X-ray pattern. This process may be aided by the geometrical construction of the locus sphere (*Lagenkugel*), and reflection circles of Polanyi,[1] Polanyi and Weissenberg,[2] and Mark and Weissenberg,[3] and of the plane polar figures (*flachenpolfigur*) of Franz Wever.[4] R. M. Bozorth[5] solves X-ray patterns from metals having a single preferred orientation by means of a series of charts which when placed over the X-ray pattern give directly certain angular relationships, between the crystal planes and the surface of the specimen.

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† Fundamental Research Division, Research Department, New Jersey Zinc Co.

[1] M. Polanyi: The X-ray Fibre Diagram. *Ztsch. f. Phys.* (1921) **7**, 149.

[2] M. Polanyi and K. Weissenberg: X-ray Fibre Diagram. *Ztsch. f. Phys.* (1922) **9**, 123; *ibid.* (1922) **10**, 41; *ibid.* (1923) **12**, 56, 78, 111.

[3] H. Mark and K. Weissenberg: Roentgenographic Determination of the Structure of Rolled Metal Foils. *Ztsch. f. Phys.* (1923) **14**, 328.

[4] F. Wever: The Structure of Rolled Cubic Crystallizing Metals. *Ztsch. f. Phys.* (1924) **28**, 69.

[5] R. M. Bozorth: Orientation of Crystals in Electrodeposited Metals. *Phys. Rev* (1925) **26**, 390.

All of these methods fail or are of difficult application when, instead of a single preferred orientation, a system of orientations exists in the metal being examined. These methods are also difficult to apply when the degree of preference is low.

A method has been devised by one of the authors, which is applicable to orientation studies irrespective of the degree of preference of orientation and which may be used where one preferred orientation, a system of orientations, or even several systems of orientations must be dealt with. Some preliminary results obtained by the use of this method were given by H. B. de Vore and W. P. Davey.[6] It is the purpose of this paper to describe the method fully and to illustrate its use in detail in the case of rolled zinc.

Outline of Method

If the specimen is thin enough to transmit the X-rays used, one pattern taken with the X-ray beam perpendicular to the surface of the specimen may suffice for a complete determination of the orientation. If the specimen is too opaque for a transmission pattern, several patterns will have to be made, allowing the X-ray beam to strike the specimen at small grazing angles. The number and nature of the patterns to be used depend on the nature of the orientation.

A diffraction pattern will show continuous diffraction rings if the crystal fragments have random orientations about the incident X-ray beam. It will show detached arcs of these rings if the crystal fragments have preferred orientations about the incident beam, and the length of these arcs is a measure of the degree of deviation from the preferred orientation. It often happens, especially with sheets of rolled metal, that of two patterns taken with different directions of the X-ray beam, one will show continuous rings and the other will show detached or semidetached arcs. We will assume for simplicity that our specimen is such a sheet of rolled metal. We will further assume (1) that one of the two patterns was taken so that a plane perpendicular to the sheet of metal and including the incident beam also includes the direction of rolling, i. e., in abbreviated language, the incident beam is in the direction of rolling, (2) that the second pattern was taken with the incident beam perpendicular to the direction of rolling, and (3) that one of these patterns shows continuous rings and that the other shows arcs. The changes in wording necessary in the following will be obvious in the case of both patterns showing arcs.

A silver print is made of the pattern that shows the arcs, care being taken that the print is a true "positive" without reversal of the right and left-hand sides. All determinations of preferred orientations by

[6] H. B. de Vore and W. P. Davey: Preferred Orientation in Tungsten. *Phys. Rev.* (1928) **31**, 160.

this method are best made with the aid of positive prints, no work being done on the original negative.   The diffraction rings are numbered consecutively in ink on the positive print, the separate arcs in each ring being distinguished by subscripts.   From a knowledge of (1) the X-ray wave length used, (2) the specimen-film distance, (3) the diameter of the diffraction rings, and (4) the crystal structure of the specimen, the Miller indices are calculated for the atomic planes in the specimen corresponding to each diffraction ring.   These indices are tabulated with the numbers of the rings to which they belong.   In this general discussion, the planes will be called by the numbers of the rings they produce. This will avoid cumbersome phrases.

A large model of the crystal lattice of the metal undergoing examination is constructed with balls and rods (Fig. 1). The balls are preferably spaced 3 to 4 in. apart, and they must be carefully placed so that the model has the true proportions of the crystal lattice which it represents.   The model is mounted on an adjustable mounting, as shown in Fig. 2, or it is attached to a double set of gimbals.   The positive print mentioned above, which shows the arcs, is mounted in a vertical position at a convenient height, and the model is set up in front of it as shown in Fig. 2.   A string is stretched from a vertical support to the model so that its direction is perpendicular to the plane of the positive print.   This string represents the incident X-ray beam.   It is maintained perpendicular to the print throughout the interpretation process.

FIG. 1.—ZINC LATTICE MODEL AND MOUNTING.

The position of the model may be adjusted without causing slack in the string if a stout rubber band is tied to one end.   In some cases it is convenient to replace the string by a narrow elastic tape.

The fact that the diffraction pattern which we have just mounted in front of the model has detached arcs shows that we have preferred orientations about an axis which is parallel to the string.   Only a slight error is introduced into the final result if we substitute the projection

of the direction of the string on the surface of the specimen.   For convenience it is called the axis parallel to the string.   It is inherent in the experimental set-up that the path of the X-ray beam for the other, unmounted, diffraction pattern is perpendicular to the path of the beam that is represented by the string.   For convenience, this X-ray path will be called "the axis perpendicular to the string."   The fact that the unmounted diffraction pattern has continuous rings shows that we have random orientation of our model about the axis perpendicular to the string.

The model is now turned to such a position that the atomic plane corresponding to ring 1 is at the correct angle to the string to account for diffraction to the center of some one arc of ring 1.   The degree of deviation in the actual sample from the medium orientation as represented by the model may be found by simple calculation from the length and the radius of the arc on the diffraction pattern.
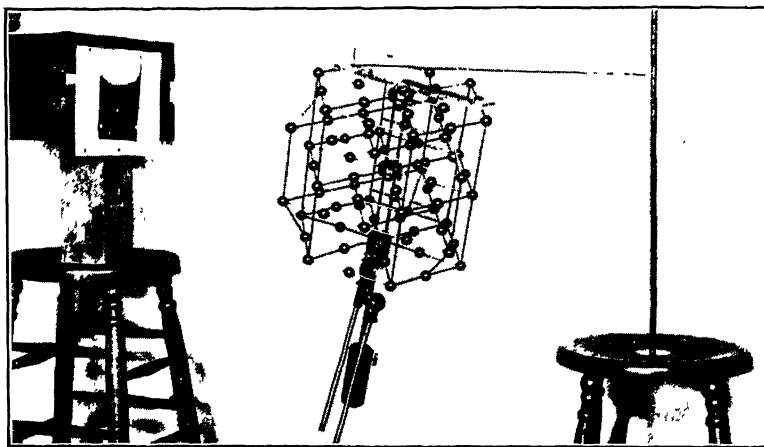
FIG. 2.—ARRANGEMENT OF APPARATUS FOR INTERPRETATION OF A PATTERN OF ROLLED ZINC.

We have now fixed the median location of plane 1 but we have not found how this plane is oriented about an axis perpendicular to itself. Therefore the model is rotated about an imaginary line normal to plane 1 until one of the planes corresponding to ring 2 comes to the correct angle for diffraction to one of the arcs in ring 2; if necessary, it is rotated, besides, about the axis perpendicular to the string until plane 2 is in the correct position for diffraction.   It must be possible to account for the total degree of deviationfrom the median orientation for the arc in ring 2 in terms of (1) a random orientation about the axis perpendicular to the string and (2) the degree of deviation for the arc used in ring 1.   If this cannot be done, we have four possibilities: (1) there are two preferred orientations and certain arcs overlap, (2) two differently orientated planes of this same family can produce overlapping rings

when the degree of deviation is taken into account, (3) two families of planes happen to have the same interplanar spacing (this can be found by direct calculation from the crystal lattice), (4) we have tried to correlate the wrong pair of arcs in rings 1 and 2.

When an orientation of the model is found that will account for one pair of arcs in rings 1 and 2, the model must be examined to see whether other members of the same families of planes can produce arcs in their respective rings (taking the degree of deviation into account). It is obvious that if we have the correct median orientation of our model, no arcs will be possible except those actually found in the diffraction pattern. Remembering (1) that for any given plane we may have *any* angle of tilt about the axis perpendicular to the string, and (2) that we may tilt the model about an axis parallel to the string to the extent permitted by the degree of deviation of the arc in ring 1, we must now investigate rings 3, 4, 5, and so forth. In every case we must check back by means of the degree of deviation to make sure that we have started with the right pair of arcs in rings 1 and 2.

If it turns out that all the rings on the diffraction pattern can thus be accounted for and that there are no theoretical arcs not shown on the diffraction pattern, we have found in our rolled sheet a single preferred orientation, with a known degree of deviation, about an axis parallel with the string, and this preferred orientation must coexist with a random orientation about the axis perpendicular to the string. If, on the other hand, it turns out that we can account for all the theoretical arcs associated with this preferred orientation but have some arcs left over on the diffraction pattern which have not been accounted for, we must cross off those already accounted for and repeat the above technique on the remaining arcs, in the hope of finding a second preferred orientation coexisting with one already found.

INTERPRETATION OF PATTERNS FROM A PARTICULAR SPECIMEN

A specimen of zinc which had been hot-rolled from 0.5 to 0.1 in. and cold-rolled from 0.1 to 0.006 in. was selected for examination.

With the X-ray beam grazing the surface of the specimen at an angle of 10° two X-ray patterns were taken. In the first case (Fig. 3) the X-ray beam was perpendicular to the rolling direction. This diffraction pattern shows distinct arcs and is therefore the one to be mounted for purposes of determining the preferred orientation of the specimen. In the second case (Fig. 4) the X-ray beam was in the plane formed by the rolling direction and the normal to the rolling plane; *i. e.*, in abbreviated language the X-ray beam was in the direction of rolling. This pattern shows continuous arcs and is therefore the "unmounted" diffraction pattern.

The model, pattern and string were set up, as previously described (Fig. 2) and the model mounting was tilted away from the pattern so that

the base of the mounting made an angle of 10° with the string. The base of the mounting therefore corresponds to the surface of the specimen. The model is attached to a series of clamps so that it may be rotated about the central hexagonal axis of the model or rotated about two axes perpendicular to and parallel with the string. This means that one axis is

FIG. 3.—ROLLED ZINC. X-RAY PERPENDICULAR TO ROLLING DIRECTION.

perpendicular to the rolling direction and one is parallel to it. Both axes are parallel to the surface of the specimen. Any of these motions can be made independently of the others. With the pattern (which was taken with the X-ray beam perpendicular to the rolling direction) in place, the model was oriented so that the basal plane (00.1) made the
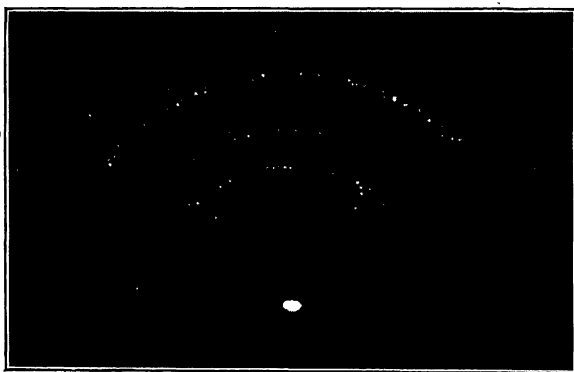
FIG. 4.—ROLLED ZINC. X-RAY IN ROLLING DIRECTION.

proper angle for reflection on an intermediate point of the arc l_2 (Fig. 5). This was done by satisfying two conditions: (1) the string (always perpendicular to the positive print of the diffraction pattern) must make an angle of 8.3° with the basal (the 00.1) plane and, (2) the string must be in the plane defined by the center of the arc l_2 and the normal to the

00.1 plane of the model. This normal was represented by a brass rod
mounted on a strip of wood which was laid on the 00.1 plane of the model.
When the correct position of the 00.1 plane was found, the model was
locked in position on the hinged mounting (Figs. 1 and 2). Rotation
of the model about the hexagonal axis (*i. e.*, the normal to the 00.1
plane), brought this 10.1 plane into proper position to "reflect" in the
2_1 arc. From this step on the only adjustment of the model was to
rotate it about the rolling direction (about the axis perpendicular to
the string), always maintaining the same relation to the rolling direction
as was fixed by the first two steps of the procedure. This rotation may
be of any angle since, from Fig. 4, a random orientation exists about the
rolling direction. The 00.1 (2) and 10.0 and 00.1 (4) reflections do not
show in Fig. 4. It was found, by manipulation of the model, that the
absence of these two reflections was consistent with the system of orienta-
tions tentatively decided upon above.
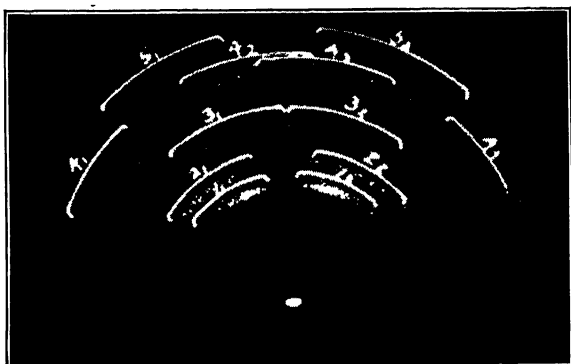
FIG. 5.—PATTERN OF FIG. 3 MARKED TO INDICATE ARCS.

NUMBERING OF AXES	PLANES
1	00.1 (2)
2	10.1
3	10.2
4	{ 10.3 { 11.0
5	00.1 (4)

By rotating the model about the rolling direction a few degrees, the
model was brought in position to reflect from the 10.2 plane on one of the
intermediate spots of 3_1. In a similar manner two 10.3 planes can be
brought to reflect on arcs 4_2 and 4_4. The diffraction rings of the 11.0
planes, if present, would have been coincident with those of the 10.3
planes. The model shows that no 11.0 planes can possibly reflect, no
matter how much the model is rotated about the rolling direction.
An intermediate spot on the arc 5_2 can also be accounted for. It was not
thought wise to consider the 11.2 arc, since it is poorly defined.

This process was twice repeated from the beginning, except that the starts were made from each of the two extremities of arc 1_2. In this manner the corresponding extremities of arcs 2_1, 3_1, 4_2, 4_4 and 5_2 could be accounted for. It is allowable to assume that every spot in these arcs could be accounted for by the system of orientations limited by the extremities of these arcs.

If the model is rotated about the rolling direction so that it points downward instead of upward, or is turned 180° in the rolling plane about a normal to the rolling plane (these rotations accomplish the same result), the model is then in a position to account for arcs 1_1, 2_2, 3_2, 4_3, and 5_1. This was carried out exactly as described for the other arcs, taking three spots on each arc.

Arcs from the 10.0 plane on Fig. 3 and the 00.1 (2) 10.0 and 00.1 (4) planes on Fig. 4 do not appear. This was found to be consistent with the system of orientations defined by the arcs that do appear.

The variation from one end of each of the arcs 1_1 and 1_2 to the other end of each is 36°. The position of the model at the mean of these is such that the hexagonal axis makes an angle of 61° with the rolling direction and that an X-axis (edge of one of the hexagonal bases) is perpendicular to the rolling direction.

The system of orientations, therefore, which exists in this specimen of rolled zinc, is such that the hexagonal axis is at an angle of 61° ± 18° with the rolling direction. There is no preferred orientation with respect to the rolling plane. Crystals exist at any position about the rolling direction, so long as their hexagonal axes have the proper relation to the rolling direction.

The authors do not wish to imply that all rolled zinc exhibits a similar type of preferred orientation. Subsequent work on other specimens of rolled zinc has shown that a different type of orientation is possible. The results herein described are from one sample only and are offered not in order to discuss the effect of mechanical working on the preferred orientations of zinc crystals but merely as a concrete example of the application of the method.

DISCUSSION

P. D. Merica, New York, N. Y.—The authors have given us a simplified method, although it may not seem to some of us too simple, for determining preferred orientation in rolled and other metals, the importance of which we are beginning to realize in an increasing measure. In the past it was the custom to regard the effect of cold work on rolled metal as being determined by the amount of cold reduction which had been put upon the material. We have realized for some time, however, that properties of cold-worked metals may vary, depending upon the way in which the cold work has been done and the metal has flowed, and recent studies have indicated that a part of that difference may be ascribed to preferred orientation of the grains. So that it is particularly opportune to have presented to us simplified and easier methods for making this determination.

A. ST. JOHN, New York, N. Y.—When I read this paper the first time I had difficulty in visualizing the mechanism that was carried out in selecting the portions of the different rings. I think I begin to see it now, and I think it is a distinct contribution to the valuation of orientation patterns. I want to inquire, however, whether I have a correct picture of the procedure. As I understand it, the first ring of Fig. 5 with its localized spots represents the pattern due to all of the particles which are favorably placed for any sort of first order reflection from the 00.1 or basal planes; that the second, say the one marked 2_1, represents a contribution from those of the particles we have already referred to, which are also favorably placed for reflection in that direction; certain others will be favorably placed for reflection in the 2_2 and so on. In other words, each particle gives rise to a contribution to a portion of the first ring, and of some other ring.

Naturally, we would rather expect the total contribution in the first ring to be much stronger than the contributions in the other rings. That is borne out by the general character of the patterns. I am not yet certain whether the rest of the picture is entirely true—as to whether or not, for instance, there may be particles which are not quite favorably placed for reflection into the first ring, and yet are favorably placed for reflection into some of the other rings; that is, the orientation is not thoroughly complete. It is merely approximate for the basal planes. I would inquire, therefore, whether that matter has been taken into consideration, and whether there is any evaluation of that in connection with its method.

M. L. FULLER, Palmerton, Pa.—It is evident from the geometry of the situation that any one crystal cannot possibly give rise to diffraction effects on every arc. Crystals that gave rise to the diffraction effects on ring 1 may not necessarily give the diffraction effects on ring 3. Each one of the arcs is made up of reflections from crystals that lie within the system of orientations described, but not from one crystal or a number of crystals orientated in exactly the same manner. Although the X-ray beam strikes a large number of crystals, not all of them are recorded on the X-ray pattern, because many of them will not be in the proper position for reflection.

W. P. DAVEY.—Two sentences at the bottom of page 559 were mixed up. They are correct in the paper now.

As indicated, there will be only a negligible error introduced if we happen to use the projection of the direction of the string on the surface of the specimen instead of using the direction of the string itself. That is a condition which we often have in determining the preferred orientation of crystals in a specimen. It is not always convenient to rotate the specimen about the direction of the original X-ray beam, but it is often convenient to rotate the model about the direction which represents the original surface of the specimen. The point we want to make is that the error introduced by that is negligibly small within the angular range with which we ordinarily have to do, and that is inherent in the solid geometry of the set up.

E. C. BAIN, Kearny, N. J.—This method of determining orientation appears the more attractive in that it is done simultaneously with a practical demonstration of the manner in which the diffraction image is formed, a real model is constructed, actual angles are introduced into the model and one arrives ultimately at the orientation which must have existed to produce the specific pattern recorded. Such practical, large-scale, synthetic methods are much more acceptable and indeed simpler to most minds than the abstract methods involving only the film and somewhat more involved mental processes.

X-ray Notes on the Iron-molybdenum and Iron-tungsten Systems

By E. P. Chartkoff* and W. P. Sykes,† Cleveland, Ohio

In 1926 one of the authors published researches on the determination and description of the iron-tungsten and iron-molybdenum systems,[1] including the equilibrium diagrams. In 1929, further work was carried on, including the examination by X-rays, which is recorded here. Measurements were made of changes in lattice parameters in the solid solutions. Precipitation from the solid solution and the accompanying changes in hardness were studied as well as the formation of the intermetallic compound phases upon sintering a mixture of metal powders.

Materials

All the specimens were prepared from the same quality of metals and by the same methods as were described in the determination of the constitutional diagrams. The metal powders as mixed and pressed were sintered or fused in a hydrogen atmosphere and subsequently treated as indicated in the titles of the figures.

The formation of the iron-rich solution in the solid was accomplished by sintering in hydrogen for a period of 20 to 30 hr. at a temperature 25° to 50° C. below the melting point of the eutectic. The tungsten-rich and molybdenum-rich solid solutions of iron were prepared by adding the iron as a solution of iron ammonium oxalate to the oxide of tungsten or molybdenum, followed by a hydrogen reduction. This method results in a homogeneous alloy after sintering the pressed metal powder for 20 to 30 hr. at a temperature slightly below that of the peritectic reaction in the system involved.

For X-ray examination the specimens were variously prepared, depending on the nature of the sample and what it was desired to show. For example, the iron containing tungsten or molybdenum in solid solution was cut with a file, the chips were put through bolting cloth, and this powder of filings formed the specimens for comparative study. The

[1] W. P. Sykes: The Iron-tungsten System. *Trans.* A. I. M. E. (1926) **73**, 968.
The Iron-molybdenum System. *Trans.* Amer. Soc. Steel Treat. (1926) **10**, 839.

molybdenum-rich or tungsten-rich solid solutions were cut into strips offering an edge approximately ½ mm. wide and 5 mm. broad, and this narrow edge surface was used for comparative study. Then a large number of the specimens were examined in block form by preparing an edge as on the strips.

LATTICE PARAMETERS

Lattice parameter measurements were made directly on the films. Each film contained the pattern of the alloy to be measured and that of the standard metal superimposed upon it (Fig. 1). For the iron-rich solid solutions, molybdenum was used as the standard, and for the tungsten and molybdenum solid solutions the iron was used as the standard. These metals were taken from the same lots of metal from which the alloys were prepared.
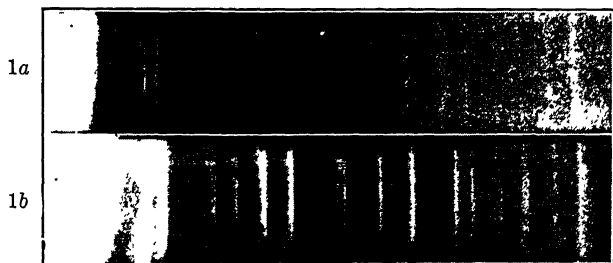
FIG. 1.—a. PATTERN OF FE + 30 PER CENT. W ALLOY, QUENCHED FROM 1520° C., AND PATTERN OF MO STANDARD. b. PATTERN OF FE PURE METAL AND PATTERN OF MO STANDARD.

In both a and b the Mo standard is the smaller pattern; that, is, the first, third, fifth, etc. lines belong to Mo.

The measurements were made on a comparator and read to the nearest tenth of a millimeter. From these measurements were calculated the angles of diffraction to each plane and the ratios of the sines of angles between planes of the same indices.

Distances as measured, from undeviated beam to the diffraction lines are designated by l.

$\theta = l \times 0.277$, where 0.277 is a constant determined by apparatus, and the classic equation $n\lambda = 2d \sin \theta$ gives the relation between the angle of diffractions θ and the interplanar distance d.

$$\frac{\sin \theta_2}{\sin \theta_1} = \frac{d_1}{d_2} = \frac{a_1}{a_2} = \text{ratio of } \frac{\text{size of unit of standard}}{\text{size of unit of alloy}}.$$

This ratio $\dfrac{d \text{ standard}}{d \text{ alloy}}$ was then compared with $\dfrac{d \text{ standard}}{d \text{ pure metal}}$ and the direct ratio in percentage was derived of $\dfrac{d \text{ pure metal}}{d \text{ alloy}}$.

On all films at least three ratios and in many cases four ratios were calculated, which were averaged to give the determination for that film. This method eliminated the major error of having separate zero points for the alloy ratio and the pure metal ratio.

Briefly describing the ranges of solid solubility of these systems from the earlier work, it may be noted that iron holds as a maximum about 33 per cent. tungsten and about 22 per cent. molybdenum. The molybdenum dissolves some 12 per cent. iron in the solid state at elevated temperatures and retains about 6 per cent. iron at room temperature. On the

ENLARGMENT OF THE IRON LATTICE BY TUNGSTEN HELD IN SOLID SOLUTION
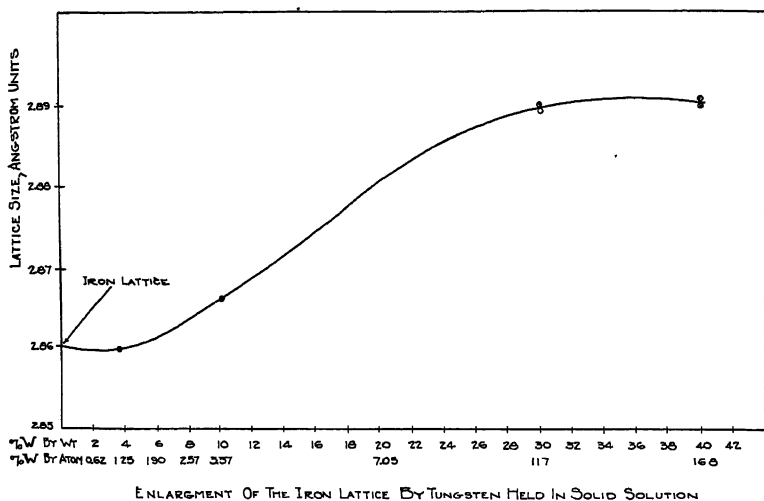
FIG. 2.—CURVE OF SOLUBILITY.

other hand, tungsten appears to hold in the solid but about 1 per cent. iron at the peritectic temperature 1650° C. No decrease in solid solubility at lower temperatures has been proved.

The curve in Fig. 2 shows the solid solubility of tungsten in iron. In terms of the size of the unit cube, it shows the progressive enlargement of the iron lattice with the increase of tungsten in solid solution till the point of saturation is reached. Beyond this point additional tungsten does not further affect the lattice size. As may be noted, when saturation occurs, the increase in cube dimension of the iron is about 1.05 per cent. The tungsten content is approximately 33 per cent. by weight, or 12 atoms per cent.

Iron seems to be able to hold approximately the same atomic percentage of molybdenum at its limit of solid solubility, but apparently the lattice expands 1.30 per cent. at saturation. Tungsten, holding about 1 per cent. by weight of iron (3.2 atoms per cent.) in solid solution at

room temperature has its lattice enlarged 0.50 per cent. The molybdenum lattice, on the other hand, shrinks approximately 0.90 per cent. with 12 per cent. by weight of iron (20 atoms per cent.) in solid solution. The measurable enlargement in parameter of the tungsten lattice by the addition of 3.2 atoms per cent. of iron represents a somewhat unusual case. Such an alloy when prepared by the method described appears to be a solid solution approaching true equilibrium. If slightly more than 1 per cent. by weight of iron is present, a small quantity of the iron-rich excess phase remains visible and constant in amount after heating for 50 to 100 hr. at about 1600° C. The microstructure of such an alloy is shown in Fig. 6.

If, in forming the solid solution the smaller iron atom replaces the larger tungsten atom at points of the tungsten lattice, a decrease in the parameter of the tungsten lattice might be expected. Such an arrangement would result in a solid solution, the density of which can be calculated.

Using Davey's value,[2] 3.155 Å for the lattice constant, the calculated density of pure tungsten is 19.32. The lattice constant is increased 0.5 per cent. by the addition of 1 per cent. of iron to 3.170 Å. This results in a theoretical density of 18.61 for the solid solution on the basis of substitution. The calculated density for a solid solution of this composition, in which the iron atoms occupy interstitial positions, is 19.23.

Density determinations were made upon two specimens of the tungsten containing 1 per cent. iron. They had been prepared by the method described above and heated for 50 hr. at 1600° to 1640° C. The density of one specimen was 19.18 and of the other 19.25. These values are the averages of three determinations in each case.

Pure tungsten as prepared commercially for working has an abnormally low density (17.5 to 18.5). After a moderate amount of working the density approaches the theoretical value of 19.3. Several density measurements made upon pure tungsten which had been reduced about 80 per cent. in cross-section by swaging, resulted in values lying between 19.17 and 19.27.

The foregoing data indicate that the iron atoms in this solid solution occupy interstitial positions instead of replacing the tungsten atoms in the lattice points.

INTERMETALLIC COMPOUNDS

In the iron-molybdenum system there appear to exist two phases corresponding to the intermetallic compounds Fe_3Mo_2 and $FeMo$. The

[2] W. P. Davey: The Lattice Parameter and Density of Pure Tungsten. *Phys. Rev.* (1925) **26**, 736.

latter was first reported by Takei and Murakami.[3]   These phases can be identified as metallographic constituents, and that corresponding to the formula FeMo (63 per cent. Mo) is stable only at temperatures above about 1200° C.   In the system iron-tungsten the intermetallic compounds Fe_3W_2 and Fe_2W and have been reported.[4]

A large number of specimens within the ranges of composition involving these intermetallic compounds were subjected to X-ray examination, using as specimens sintered blocks and metal filings.   It became evident
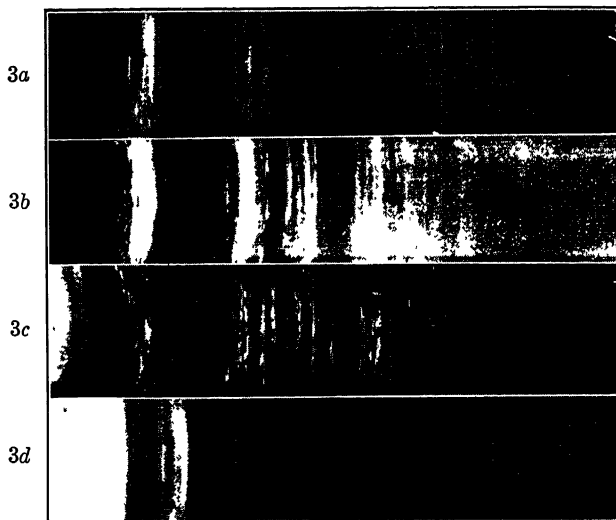
FIG. 3.—*a.* FE + 53 PER CENT. Mo, SINTERED 10 HR. 1400° C., 2 HR. 1500° C. COOLED TO 500° C. IN 1 HOUR.   *b.* FE + 62 PER CENT. Mo, SINTERED 12 HR. 1400° TO 1450° C.   HEATED TO 1500° C. 30 MIN. AND QUENCHED.   *c.* FE + 69 PER CENT. W, PREVIOUSLY FORMED BY LONG SINTERING AT 1550° TO 1600° C.   HEATED TO 1000° TO 1100° C. 12 HOURS.   *d.* FE + 62 PER CENT. W, SINTERED 24 HR. 1450° TO 1500° C.

at once that the complexity of the resulting diffraction patterns would seriously limit the conclusions to be drawn therefrom.   The complete solution of the composition ranges involving these intermetallic compounds must be in itself the subject of a separate report.   It is sufficient to state here that the diffraction patterns of the alloys in these ranges are typified by several groups of many lines each, indicating a crystal system of low order of symmetry and large dimensions.   Typical patterns are shown in Fig. 3, corresponding to the intermetallic compounds Fe_3W, Fe_2W, Fe_3Mo_2 and FeMo, each one representing metallographically a single phase.   There are only slight differences among these patterns.

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[3] T. Takei and T. Murakami: On the Equilibrium Diagram of the Iron-molybdenum System.   *Trans. Amer. Soc. Steel Treat.* (1929) **16**, 3, 339.

[4] H. Arnfelt: On the Constitution of the Iron-tungsten and Iron-molybdenum Alloys.   *Carnegie Scholarship Memoirs*, Iron and Steel Inst. (1928) **17**.

LOW-TEMPERATURE PRECIPITATION OF INTERMETALLIC COMPOUND PHASE
FROM SOLID SOLUTION

The supersaturated solid solution of tungsten in iron when reheated at about 700° C. for some time increases in hardness, as has been previously reported. The first change in microstructure accompanying this hardness increase is a general and rapid darkening of the polished section upon etching, as shown in Fig. 5b. The massive precipitate
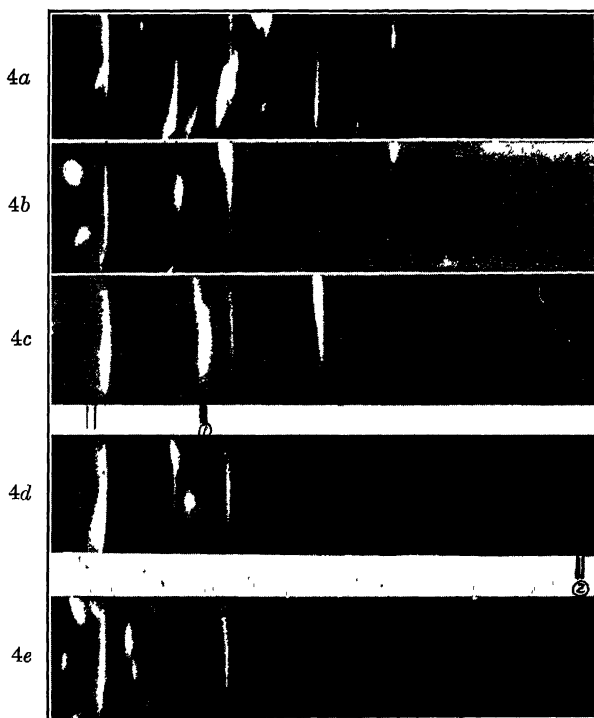
FIG. 4.—a. FE + 25 PER CENT. W, AS QUENCHED, FROM 1520° C. ROCKWELL HARDNESS, 14. b. FE + 25 PER CENT. W, AGED 60 HR. AT 600° C. ROCKWELL HARDNESS, 16. c. FE + 25 PER CENT. W, AGED 5 HR. AT 700° C. ROCKWELL HARDNESS, 48. d. FE + 25 PER CENT. W, AGED 40 HR. AT 800° C. ROCKWELL HARDNESS, 39. e. FE + 25 PER CENT. W, AGED 12 HR. AT 1000° C. ROCKWELL HARDNESS, 25.

outlining the grain boundaries was formed during cooling from 1500° to 1450° C. before quenching from the latter temperature. By quenching from 1500° C. it is possible to retain 25 per cent. of tungsten in solid solution, as is shown in Fig. 5a.

The specimens used in this part of the X-ray study were all sintered for 15 to 20 hr. at 1475° to 1500° C. and water quenched from 1500° C. They were then reheated at the temperatures shown in Table 1 for periods of time varying from 1 to 200 hr. The maximum hardness was developed
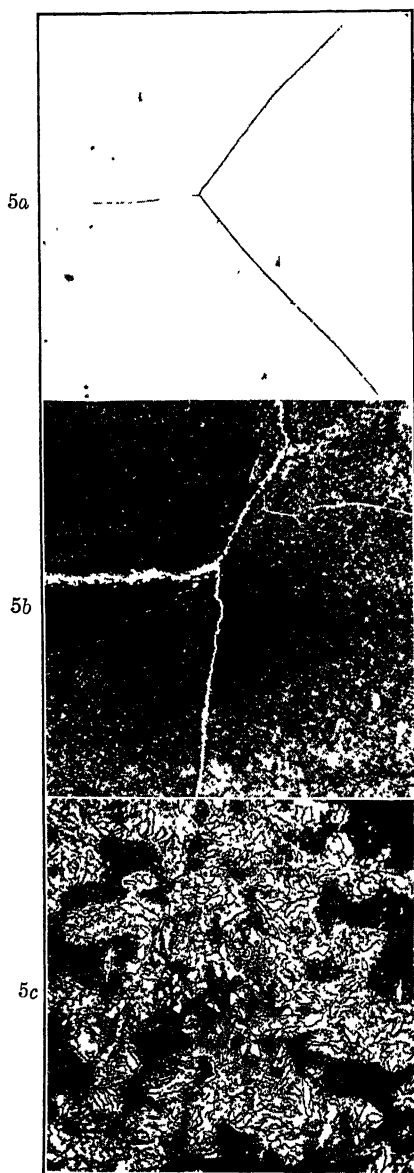
FIG. 5.—*a*. FE + 25 PER CENT. W, AS QUENCHED. × 500. *b*. QUENCHED AND AGED 5 HR. AT 700° C. × 500. ⅓ REDUC. *c*. QUENCHED AND AGED 12 HR. AT 1000° C. × 500.

These metallographic views correspond to films in Fig. 4*a*, *c*, *e*. Reduced ⅓; original magnification given.

after 5 hr. heating at 700° C. In the diffraction patterns, Fig. 4, certain lines of the precipitated phase are clearly visible. The microscope, however, fails to resolve the particles of this phase at 1000 magnifications, the etched section showing only a general darkening as has been stated.

The diffraction pattern of the solid solution as quenched from 1520° C. is shown in Fig. 4*a*, with the body-centered cubic pattern of iron reproduced below. A considerable strain in the lattice is indicated by the flares and the nonuniform character of the lines.

By reheating the quenched alloy at 600° C. for 60 hr., the hardness is increased slightly but there occurs no marked change in the diffraction pattern, Fig. 4*b*. After heating at 700° C. for 5 hr., a new phase appears, marked in the diffraction pattern 4*c* by the broad band and two faint lines at the extreme left of the pattern. This diffuse band represents a group of lines of which three are well resolved by heating at higher temperatures as shown in 4*e*. The diffuse character of the first noticeable diffraction from the second phase in 4*c* is typical of extremely minute crystals, and in this case corresponds to the condition of maximum hardness in this series. The corresponding microstructure is shown in Fig. 5*b*.

When reheated at 800° and 1000° C. the particles of the precipitated phase rapidly attain visible size and the lines of this phase in the pattern increase in number and degree of resolution. Photomicro-

graph 5c corresponds to the pattern 4e, in which the most prominent lines of the precipitate are marked.

TABLE 1.—*Hardness Chart*

Rockwell "C" Hardness

Fe + 25 Per Cent. W Alloy Quenched From 1500° C. and Aged

Hardness of Alloy as Quenched-C-14

Aging Hours	Temperature of Aging, Deg. C.			
	600	700	800	1000
1	C-14	C-35	C-46	
5		C-48	C-45	
12				C-25
20		C-47	C-42	
40			C-39	
60	C-16			
200	C-27			

The difference in character between the lines at the extreme right of the patterns 4a and 4d appears to be significant.

In 4a, this diffraction from the quenched and relatively soft solid solution is diffuse and nonuniform, indicating a strained condition of

FIG 6.—W +1.10 PER CENT. FE. SINTERED AT 1600° to 1640° C. FOR 50 HR. × 500
Reduced ⅓; original magnification given.

the crystal lattice. In pattern 4d, it appears as a well-resolved doublet characteristic of a lattice free from strain. Since the latter pattern is that of the harder material it may be concluded that the increased hardness of 4d is due primarily to the presence of the precipitated phase rather than to any strained condition of the solid solution lattice.

DISCUSSION

K. R. Van Horn, Cleveland, Ohio (written discussion).—It is interesting to note that the authors have obtained lines from precipitated constituent in an aged iron-tungsten alloy. Lines due to $CuAl_2$ have been found in an aged specimen of duralumin by Schmidt and Wassermann. $CuAl_2$ lines have been obtained from an aged binary Al-Cu alloy, in the laboratory of the Aluminum Co. of America. Masing observed lines due to precipitate in aged Be-Cu alloys. The precipitate in the iron-tungsten alloy is particularly interesting because the reflections were coincident with maximum hardness.

The authors have pointed out that in a 25 per cent. tungsten alloy the specimen of maximum hardness has less internal strain or lattice distortion than the softer quenched specimen. Evidently this is one case in which the hardening can be attributed almost entirely to a precipitated phase.

L. W. McKeehan, New Haven, Conn.—With regard to Fig. 2 the author states that the solubility limit of tungsten in iron is reached somewhere between the last two points on his curve. If there is other evidence that such a solubility limit is reached it would be reasonable to remove the hump in the curve between the second and third points. The first three points lie well enough on a straight line. One would prefer to have such a straight line, if justified in any way, and to allow a change in slope to appear in the neighborhood between 30 and 40 weight per cent. tungsten, rather than showing the curve smooth in that region. There may be reasons for not doing this which are not presented in the paper, and I would like to hear about them if they exist.

The iron point, which is derived from the measurements of others, has to be forced on to the curve by tipping it up at the origin. It is just possible that this indicates a constant error in the lattice determinations for the other points, and if so the curve from zero tungsten up might be a straight line also.

W. P. Sykes.—Dr. McKeehan's point is well taken. The microstructure of these alloys shows that iron is saturated with tungsten in the solid with about 30 per cent. of tungsten at the eutectic temperature. Consequently the curve in Fig. 2 should properly be drawn as Dr. McKeehan suggests.

The System Cadmium-mercury*

By Robert F. Mehl‡ and Charles S. Barrett,† Anacostia, D. C.

THE system cadmium-mercury has attracted much attention, chiefly because of its importance in the study of electrochemical standard cells. The constitutional diagram, as it is accepted today, is essentially that
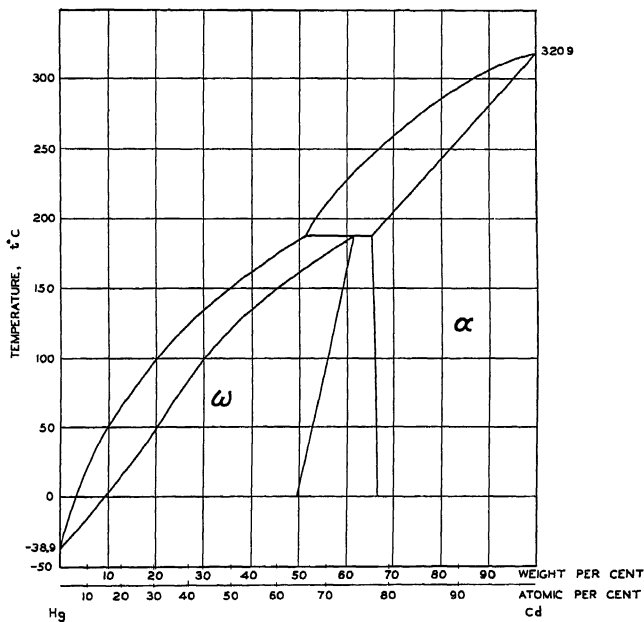
FIG. 1.—BIJL'S DIAGRAM FOR CADMIUM-MERCURY ALLOYS.

developed by Bijl[1] (Fig. 1), though there has been a great amount of work done on the system by other workers.[2]

A year ago the senior author published a paper on the crystal structure of the system, in which were described determinations of crystal structure

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‡ Assistant Physicist, Division of Physical Metallurgy, Naval Research Laboratory.

1 H. C. Bijl: Die Natur der Kadmiumamalgame und ihr electromotorisches Verhalten. *Ztsch. phys. Chem.* (1902) **41**, 641.

2 The bibliography on this system has been compiled by T. W. Richards, H. L. Frevert, and C. E. Teeter, Jr. See *Jnl. Amer. Chem. Soc.* (1928) **50**, 1293.

by a study of X-ray diffraction on a series of 10 alloys varying in composition from 23 weight per cent. cadmium to pure cadmium.[3] These measurements were made at ordinary temperatures, leaving uninvestigated the composition range between zero and 23 weight per cent. cadmium in which the alloys are partly or wholly liquid at room temperature.

This investigation disclosed no feature in the alloys investigated discordant with the diagram developed by Bijl. The mercury-rich solid solution (Fig. 1), between 23 and 50 weight per cent. cadmium, was found to be face-centered tetragonal, and the cadmium-rich solid solution close-packed hexagonal, indistinguishable from pure cadmium. It was pointed out, however, that the determination of the crystal structure of pure mercury at −115° C. by Mc Keehan and Cioffi[4] gave a rhombohedral structure, differing completely from the face-centered tetragonal structure found for the ω solid solution, which Bijl's diagram shows to be a terminal solid solution with pure mercury as the solvent. This result is contrary to general experience with terminal solid solutions, which uniformly show the structure type of the solvent, usually modified by lattice distortion. Two possibilities were then presented, either the crystal structure of pure mercury at its melting point is face-centered tetragonal, or the diagram proposed by Bijl is incorrect in the range from zero to 23 weight per cent. cadmium. The object of the present investigation is to furnish information on this moot point.

The cadmium-mercury system, as represented by Bijl's diagram, is quoted in most textbooks on metallurgy as the only example known of the Type IV diagram derived theoretically by Roozeboom.[5] It is, therefore, of theoretical interest to know whether or not this system actually conforms to the type of equilibrium demanded by the Type IV diagram.

CRYSTAL STRUCTURE

When this work was begun the only trustworthy determination of the crystal structure of mercury was that of McKeehan and Cioffi. Their measurements were made with the mercury at a temperature of −115° C. and were not taken over a temperature range extending to the melting point. There remained the possibility, therefore, that a transition in the solid state with ascending temperature should transform the rhombohedral form stable at a low temperature to a face-centered tetragona form stable at higher temperatures, identical in type with the structure previously found for the ω solid solution in the concentration range

[3] R. F. Mehl: Crystal Structure of the System Cadmium-mercury. *Jnl.* Amer. Chem. Soc. (1928) **50**, 381.

[4] L. W. McKeehan and P. P. Cioffi: Crystal Structure of Mercury. *Phys. Rev.* (1922) **19**, 444.

[5] H. W. B. Roozeboom: Erstarrungspunkte der Mischkrystalle zweier Stoffe. *Ztsch. phys. Chem.* (1899) **30**, 385.

23 to 50 weight per cent. cadmium. Such a circumstance would retain the equilibrium diagram of Bijl with the addition of such transitions in the solid mercury-rich alloys originating in the transition in the pure mercury as should be found by experiment.

Accordingly, X-ray diffraction patterns were taken first of pure mercury at temperatures higher than that used by McKeehan and Cioffi, and later of cadmium-mercury alloys in the range of composition previously left uninvestigated.

Materials and Method

The mercury used was commercial "redistilled mercury," purified in the accepted way by repeated passage through a nitric acid tower, and a twofold distillation at a low pressure with a constant bubbling of air through the boiling mercury. The cadmium analyzed Cd, 99.902 per cent.; Zn, 0.07; Pb, 0.027; Fe, 0.001. The measurements were made on the X-ray Diffraction Apparatus constructed by the General Electric Co., which is in such general use in this country that no description of it is deemed necessary.

All measurements were made by the "powder method." The mercury specimens were prepared by levigating small drops of mercury in an agate mortar with a high grade of finely ground flour. This mixture was packed in one-half of a Pyrex tube with a paper-thin wall of inside diameter 0.5 mm. The other half of the tube was packed with a mixture of sodium chloride and flour.

V-shaped notches were cut in the two side walls of the cassette around the small notches provided for carrying the ordinary specimen tube. Into each of these notches was rigidly clamped a short piece of Pyrex tubing, 1 cm. dia. The specimen tube·was supported between these tubes by a wire frame attached inside the tubes. This wire frame was designed to permit the rotation of the specimen tube during the exposure, though later this was found unnecessary. The specimen tube was enclosed by a collodion sleeve cemented to the ends of the glass tubes. One of the tubes was connected to a Dewar flask and the other was free to the air. The temperature desired was attained by passing a stream of oxygen gas through liquid air held in the Dewar flask and over the specimen tube, and maintained by adjusting the rate of flow of the oxygen gas. The temperature of the specimen tube was given by two calibrated iron-constantan thermocouples attached to the ends of the specimen tube. It was found, with this kind of apparatus, that the temperature difference at the two ends of the specimen tube amounted usually to about 5°, and over the mercury half of the tube to about 2.5°. A manual and periodic adjustment of a reducing valve controlling the rate of oxygen flow gave a sensitive and satisfactory temperature control,

the temperature at either junction varying only $\pm 5°$ in the usual case throughout a run.

In order to prevent the formation of ice around the collodion sleeve, which would give an additional and confusing spectrum on the film, the cassette was equipped with a pan of phosphorus pentoxide, and as a whole cemented airtight by modeling clay to the metal drum holding the X-ray bulb.

Experimental Results of Investigation

Several unsuccessful attempts were made to obtain diffraction lines from pure mercury without cooling below $-50°$ C. at any time. Lines began to appear at $-60°$ C., and were prominent on a film taken at $-46°$ $\pm 2°$ C. after a previous cooling to $-90°$. This apparent supercooling has also been noted by Wolf,[6] yet cooling curves taken on mercury in massive form indicated a sharp freezing point virtually free from any supercooling. The question whether or not the finely divided state in which mercury existed in these experiments and those of Wolf is conducive to a supercooling, absent in mercury in a massive state, can only be propounded here. No attempt has been made to answer it.

The data from the best of the powder diffraction photographs are listed in Table 1. All the lines from pure mercury can be accounted for by assuming a simple rhombohedral structure, with an axial ratio of 1.937 and $a_o = 3.460 \times 10^{-8}$ (hexagonal system of notation), thus confirming in general the results of McKeehan and Cioffi, and of Wolf, obtained at other temperatures. This structure yields a calculated density of 14.25, agreeing satisfactorily with the density of 14.193 at $-38.8°$ found by Mallet[7] and of 14.383 at $-188°$ found by Dewar,[8] which yield on interpolation a density of 14.20 at $-46°$. The calculated and observed densities are in better agreement using the data obtained here than by using the data of McKeehan and Cioffi, and are within the probable experimental error.

It is probable that the lines observed here are those characteristic of solid mercury at its melting point, since cooling curves revealed no thermal critical point in the solid state. In order to prevent an accidental melting and a subsequent possible undercooling during the exposure to X-rays, the temperature on the specimen was run down to $-90°$ C. and brought back to $-46°$ C. every $1\frac{1}{2}$ hr. during the 20-hr. exposure.

[6] M. Wolf: Crystal Structure of Solid Mercury. *Nature* (1928) **122**, 314.

[7] J. W. Mallet: On the Density of Solid Mercury. *Proc. Roy. Soc.* (Lond.) (1877) **26**, 71.

[8] J. Dewar: Coefficients of the Cubical Expansion of Ice, Hydrated Salts, Solid Carbonic Acid, and Other Substances at Low Temperatures. *Chem. News* (1902) **85**, 277.

TABLE 1.—Results of Crystal Structure Investigation[a]

Theoretical Simple Rhombohedral C = 1.94, a_0 = 3.46; d in Angstrom Units	Mercury at −46° ± 2°	Alloy with 5.2 Atomic Per Cent. Cadmium at −45° ± 5°	Alloy with 5.2 Atomic Per Cent. Cadmium at −60° ± 10°	Alloy with 10.4 Atomic Per Cent. Cadmium at −52° ± 5°	Alloy with 19.6 Atomic Per Cent. Cadmium at −42° ± 5°	Alloy with 28.1 Atomic Per Cent. Cadmium at +20°	Alloy with 28.1 Atomic Per Cent. Cadmium at +20°	Alloy with 54.3 Atomic Per Cent. Cadmium at +20°	Alloy with 54.3 Atomic Per Cent. Cadmium at −45° ± 5°	Average of Lines for ω Solid Solution (Mehl)
2.72	2.74 s	2.72 m	2.75 s	2.81 s	2.80 w	2.82 s	2.795 s	2.78 s	2.80 s	2.785 s
				2.71 s	2.72 w					
2.23	2.237 s	2.23 m	2.26 s	2.32 s	2.31 w	2.32 vs	2.315 s	2.32 vs	2.34 vs	2.327 vs
			(2.12? vw)	2.238 s	2.24 w					
			(2.01? vw)							
1.730	1.729 m	1.92? vw	1.730 m	1.999 vw	(1.97? vw)	1.981 s	1.987 w	1.96 s	1.96 m	1.966 s
		(1.67–1.73 vw)		1.724 w	(1.72? vw)					
1.464	1.466 m	1.44–1.46 vw	1.469 m	1.504 w		1.505 s	1.507 m	1.496 s	1.497 s	1.495 s
				1.460 w		(1.427? w)	1.425 vw	1.446 w	1.440 vw	1.438 w
				1.417 w		(1.399? w)				
1.369	1.370 m	1.32–1.37 vw	1.369 w	1.368 w		1.279 w	1.272 vw	1.384 vw	1.378 vw	1.389 w
				1.268 vw		1.255 w		1.275 w	1.277 w	1.281 w
1.229	1.226 vw	1.23–1.24 vw	1.234 w	(1.225? vw)		1.196 w	1.194 vw	1.243 vw	1.237 w	1.239 vw
				(1.203? vw)					1.190 w	1.194 vw
				(1.184? vw)						
				(1.159? vw)						
1.120	1.120 w		(1.118? vw)	1.115 vw		1.161 w	1.158 vw	1.160 m	1.155 w	1.161 w
1.071				1.073 vw						1.020 vw
1.003	1.003 vw			1.035 vw		1.026 vw				1.000 vw
				1.005 vw		1.002 vw		1.002 vw	(1.008? vw)	
0.940	0.940 vw			0.968 vw		0.945 vw				0.941 vw
				0.942 vw						

[a] Intensities are estimated as very strong (vs), strong (s), medium (m), weak (w), and very weak (vw).

[b] The usual sodium chloride calibration was omitted in this determination.

The lines found in the powder photograph of pure mercury were also found in those of alloys with 5.2, 10.4, and 19.6 atomic per cent. cadmium. The films obtained were all poor, so that it was impossible to ascertain possible small changes in lattice parameter resulting from change in composition. With increasing cadmium content, beginning with the 10.4 atomic per cent. cadmium alloy, a second set of lines appeared, which persisted throughout the composition range marked ω in Fig. 1, as might be expected from the face-centered tetragonal lattice $a_0 = 5.570$ and $c_0 = 2.896$ Ångstrom units found by the senior author in the previous investigation. The films showing a single phase at 5.2 atomic per cent. cadmium are indicative of a terminal solid solution, equivalent in structure to pure mercury and radically different in structure from the ω solid solution. The occurrence of two sets of lines on the films for the 10.4 and 19.6 atomic per cent. alloys indicates a region of two phases. The obvious inhomogeneity of all these alloys, however, makes further or more definite conclusions regarding the phase diagram unwarranted.

If, then, there is a new solid solution terminal to mercury, and a heterogeneous range separating this and the ω solid solution, it should be demonstrable by thermal analysis. For this purpose a series of heating and cooling curves were taken.

THERMAL ANALYSIS

Method

Thermocouples were made of carefully selected constantan and iron wire, B. & S. gage No. 30. These were calibrated against the melting point of pure mercury; the ice point; a point at 30° C. against a calibrated thermometer reading to $\frac{1}{100}$° C.; and the boiling point of water corrected for barometric pressure. The cold junction of the couple was placed in ice water in a Dewar flask. The e.m.f. from the thermocouple was read on a Leeds & Northrup Type K potentiometer. All equipment was mounted on an equipotential copper surface to eliminate spurious e.m.f.'s. Temperatures were read to 0.1° C. with an accuracy of ±0.05° C. Heating curves were obtained by allowing a 30-g. sample in a Pyrex tube previously frozen in liquid air to come to room temperature in a container packed with cotton waste. The cooling curves were taken by suspending a glass tube containing the alloy in a 500-c.c. Dewar flask in such a way that the alloy came halfway between the neck of the Dewar and the surface of the liquid air, leaving a free space of 3 to 4 cm. between the bottom of the tube and the liquid air. Readings were taken from 3 to 7 times a minute. This was found completely suitable to the type of change investigated, as will appear later. The results were plotted as time-temperature curves, from which the arrest times were read off,
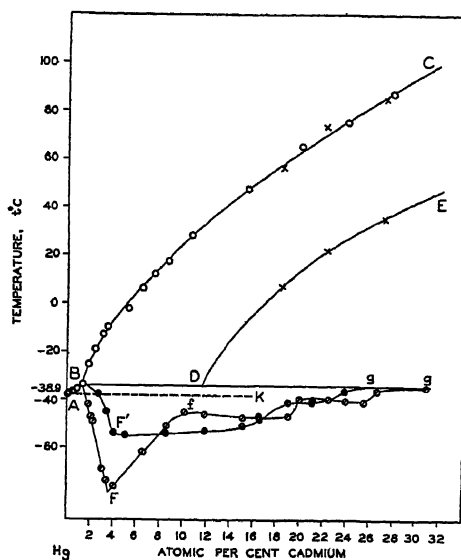
FIG. 2.—THERMAL EFFECTS IN MERCURY-RICH ALLOYS.
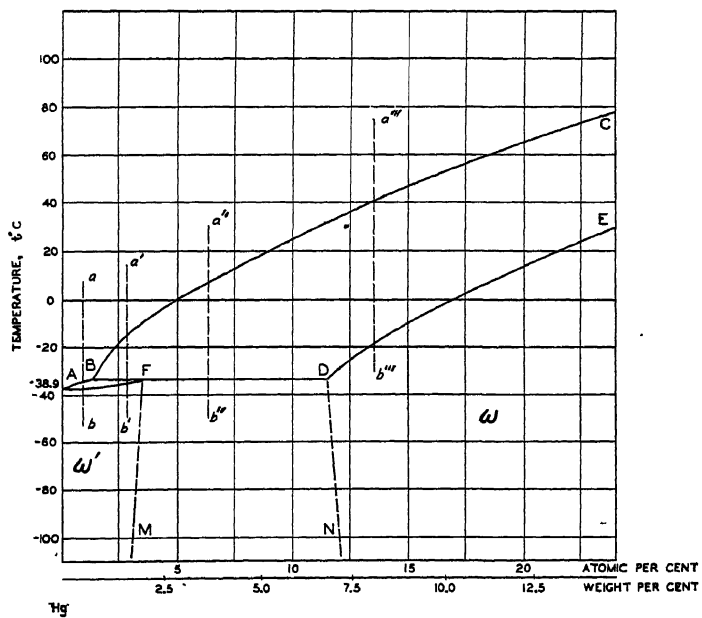
FIG. 3.—PROBABLE EQUILIBRIA IN MERCURY-RICH ALLOYS.

and as direct-rate curves, upon which the various solid-solid transitions were more easily distinguishable.

It did not appear advantageous to use more elaborate thermometric methods, since it was early evident that any thermal curve would only approximately show the true transitions, for all of the reactions taking place at these low temperatures in this system are severely restrained. This was demonstrated by a difference curve taken with copper as a comparison body, which furnished no more information than that given by the time-temperature and the direct-rate curves. Because of the greater ease in visualizing the phase changes from time-temperature and direct-rate curves, these alone were used.

The results obtained from heating and cooling curves are given diagrammatically in Fig. 2. These data appear to be most consistent with a diagram of the type given in Fig. 3 and will be discussed with this as a basis.

The Liquidus

Bijl determined no liquidus temperatures below 18 atomic per cent. cadmium. The liquidus temperatures plotted in Fig. 2 from the present work (AB and BC) were taken from the last points of inflection on heating curves for alloys between zero and 8 atomic per cent. cadmium, and the first points of inflection on cooling curves for alloys between 8 and 23 atomic per cent. cadmium. These temperatures are in satisfactory agreement with those of Bijl where the two sets of determinations overlap. The sharp point of inflection on the liquidus at 1.3 atomic per cent. cadmium is the only notable feature exhibited by the liquidus.

The Solidus

As might be expected, no trace of the solidus DE (Fig. 2) was found on any thermal curve. The line DE in Fig. 2 was drawn from Bijl's data obtained with a dilatometer. However, below $-33°$ a complicated series of transformations were evident. The 160 time-temperature curves taken may be represented by three type curves, which are given in Figs. 4, 5 and 6. The discussion of the thermal data will be built around these type curves, with observed minor variations described in detail.

Heating and Cooling Curves

Fig. 4 gives the type of heating curve obtained for alloys in the concentration range zero to 1.3 weight per cent. cadmium. It strongly suggests the existence of conjugate solidus and liquidus curves with complete miscibility in both the solid and liquid states. The occurrence of a terminal solid solution in a concentration range (up to 3.5 atomic
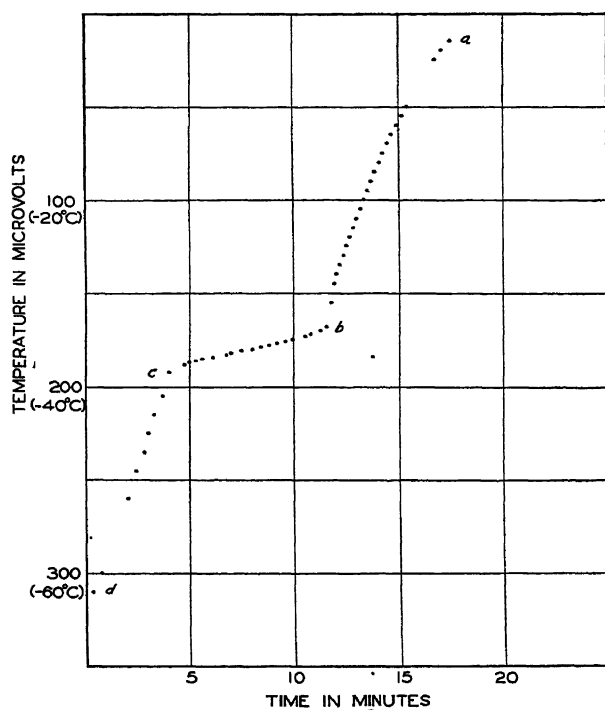
FIG. 4.—HEATING CURVE FOR 1.3 ATOMIC PER CENT. CADMIUM ALLOY.
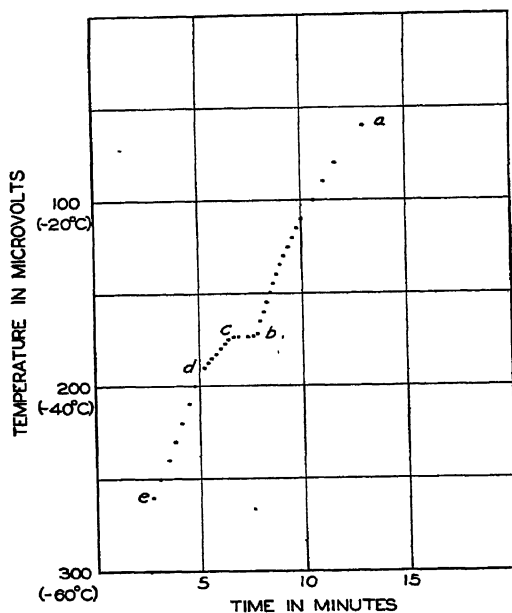
FIG. 5.—HEATING CURVE FOR 12.0 ATOMIC PER CENT. CADMIUM ALLOY.

per cent. cadmium) is also indicated by the crystal structure data, as already noted. Points b (Fig. 4) rise regularly with increasing cadmium to 1.3 atomic per cent. cadmium. Points c do not vary in temperature within this concentration range. The definition of points c, however, becomes poorer with increasing cadmium, though traces of the point may be found up to 15 atomic per cent. cadmium.

In the concentration range 1.3 to 27 atomic per cent. cadmium arrests were found on both heating and cooling curves at the temperature $-34°$ (Fig. 2). The durations of arrest on the heating curves (circles with single diameters) show a sharp maximum at 3.5 atomic per cent. cadmium. The leg BF of the duration triangle was found to be linear, but the leg Fg is irregular. The type of heating curve found in this region of concentration is given in Fig. 5. It is characterized by an arrest cb, and two distinct branches cd and de at lower temperatures. Point d in Fig. 5 is shown in Fig. 2 as a dotted line, AK, which then represents the temperature at which point c in Fig. 4 and point d in Fig. 5 were found. This temperature is constant at the freezing point of mercury throughout the concentration range in which it is found. The cooling curves in this concentration range gave durations of arrest (circles with crossed diameters in Fig. 2) which do not form as

FIG. 6.—DIRECT-RATE HEATING CURVE FOR 6.4 ATOMIC PER CENT. CADMIUM ALLOY.

sharp a maximum F' as the durations from the heating curves. This ill-defined maximum obtained from the cooling curves comes, however, at about the same composition as that obtained from the heating curves.

None of the thermal points enumerated could be found in the concentration range 28 to 70 atomic per cent. cadmium. However, a new critical point was found in this range, characterized by a point of inflection on the cooling and heating curves that was especially well defined on the direct-rate curves. The direct-rate curve obtained for the 64 atomic per cent. cadmium alloy is shown in Fig. 6. This point varied in temperature from $-14.0°$ at 24 atomic per cent. cadmium to $-10.5°$ at 70 atomic per cent. cadmium, fading out at each end of this composition range. No other thermal change was found in the alloys in this concentration range, though the curves were prolonged from $-60°$ to zero in the usual case and in individual cases over wider temperature ranges

(19 atomic per cent. cadmium from $+15°$ to $-40°$; 31 atomic per cent. cadmium from $+15°$ to $-80°$; and 34 atomic per cent. from $+40$ to $-30°$).

Discussion of Results

Fig. 3 assumes that there is a peritectic horizontal at $-34°$, a peritectic point at 3.5 atomic per cent. cadmium, a new solid solution field from zero to 3.5 atomic per cent. cadmium, a heterogeneous field extending from 3.5 to 12.0 atomic per cent. cadmium, and a solid solution field extending from 12.0 atomic per cent. cadmium to higher concentrations of cadmium.

The conjugate solidus and liquidus curves AB and AF are shown rising in temperature with increasing cadmium. The thermal points (Fig. 2) AK, however, are nearly invariant in temperature. This may be explained by a lack of equilibration in the freezing alloy relatively more severe as the solidus and liquidus curves diverge with increasing temperature. That is, through a nearly complete lack of reaction between the deposited crystal and the liquid alloy, the liquid alloy is impoverished of cadmium until the last drop solidifying has the composition of nearly pure mercury. The freezing point of mercury is thus the limiting temperature below which no liquid can exist, however incomplete the reaction.

The type of thermal curve obtained for alloys between 1.3 and 3.5 atomic per cent. cadmium (Fig. 5) is entirely consistent with the phase changes indicated along the line $a'b'$ in Fig. 3. In addition to the initial liquidus point there is a duration of arrest (BF) and then a sloping off of the curve, with the establishment of an undisturbed rate of cooling only below freezing point of mercury. The persistence of the temperature AK is to be explained in the same way as in the preceding paragraph. After the solidification of the peritectic composition, the alloy freezes as an alloy in the range zero to 1.3 atomic per cent. cadmium. For alloys between 3.5 and 15 atomic per cent. cadmium similar curves were obtained. The persistence of the temperature AK into this region is no doubt conditioned by the incompleteness of the reaction during solidification. An alloy freezing along $a''b''$ (Fig. 3) will deposit crystals rich in cadmium. With little or no reaction of the crystal with the melt, the melt becomes increasingly rich in mercury. A certain small amount of the melt will thus migrate into compositions in the range AB, producing as before a remanent of nearly pure liquid mercury solidifying near the freezing point of mercury. The temperature AK becomes increasingly less well defined with increasing cadmium, finally becoming no longer perceptible beyond about 15 atomic per cent. cadmium. This is consistent with the above explanation, since with increasing cadmium content the amount of remanent nearly pure mercury will decrease.

The selection of the proper composition for the peritectic point presents, then, some difficulty. A complete peritectic reaction demands that the solid deposited along DE (Fig. 3) react completely with the melt, forming along line $a''b''$ a solid of the peritectic composition F and a solid of the composition D, and along line $a'b'$ a solid of the peritectic composition F and a melt of the composition B. With incomplete reactions a solidifying alloy of the composition in the range BD (Fig. 3) behaves as a mixture of alloys richer and poorer in cadmium than the gross composition of the alloy. Each constituent of the mixture will precipitate the peritectic composition when the peritectic temperature is reached, but it is difficult to see any rational way to correlate the peritectic duration of arrest with heterogeneities in composition. The maximum duration of arrest on the cooling curves is indistinctly indicated at 4 atomic per cent. cadmium. The maximum on the heating curves is very sharp at 3.5 atomic per cent. cadmium, and this composition is chosen as more representative of the true peritectic composition.

The prolongation of Ff (Fig. 2) intersects the peritectic horizontal near the same point produced by the prolongation of DE (from Bijl's data). It seems likely, therefore, that the true position of point D is in the neighborhood of 12.0 atomic per cent. cadmium. The persistence of the peritectic arrest to 30 atomic per cent. cadmium, beyond the point D in Fig. 3 which is placed at 12 per cent., may be explained in similar fashion. Incomplete reaction of an alloy cooling along $a''b'''$ will preserve in the last solidifying liquid a composition relatively much richer in mercury. This liquid will, on solidification, therefore show a thermal behavior to be expected from an alloy of the type $a''b''$. The result will be a preservation of the peritectic arrest in compositions to the right of point D in Fig. 3.

Of the point of inflection on the cooling and heating curves first appearing in the intermediate solid solution at 24 atomic per cent. cadmium, at $-14°$, and extending to 70 atomic per cent. cadmium, at $-10.5°$, little explanation is offered. It is a solitary point of inflection corresponding to a change in specific heat; it is unaccompanied by any other thermal disturbance; it does not correspond to a change in phase, judging from the identical X-ray diffraction spectra obtained at temperatures above and below the point; it becomes less distinct and finally fades out towards each end of its composition range. It is here classified, without criticism, with those mysterious solid transitions in alloys which indicate a change in energy characteristics without any change in crystal structure, and is indicated on Fig. 7 by a dotted line. Although the point was found in an alloy with 24 atomic per cent. cadmium it very likely would not be found in completely equilibrated alloys under 40 atomic per cent. cadmium. It is, of course, impossible to set this limit accurately.

A more complete analysis of this system than that given above would entail great difficulty. The system does not lend itself to ordinary metallographic investigation because of the low temperatures at which the reactions take place and the resulting incompleteness of these reactions. The authors content themselves with suggesting a new and probable diagram representing the equilibrium in mercury-rich cadmium-mercury alloys, given in Fig. 7.
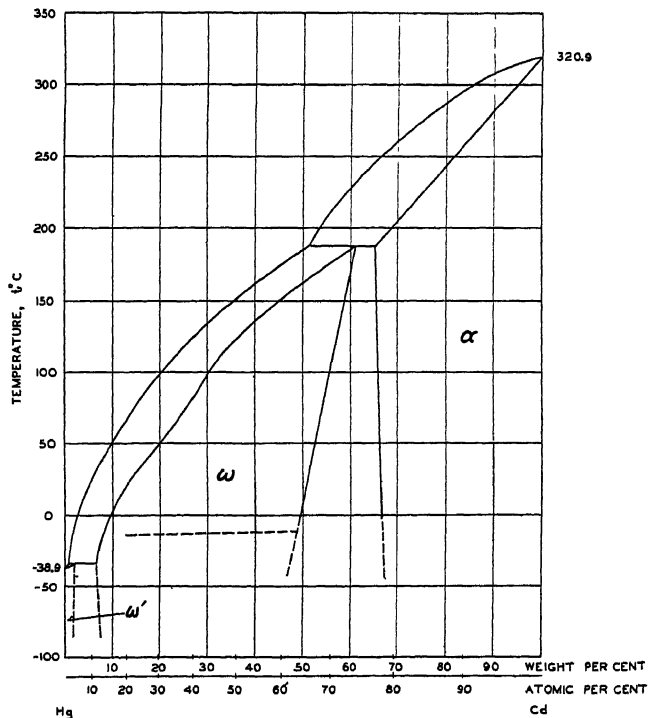
FIG. 7.—NEW CONSTITUTIONAL DIAGRAM FOR CADMIUM-MERCURY SYSTEM.

SUMMARY

1. The crystal structure of mercury at −46° was determined and found to be simple rhombohedral, in agreement with previous determinations at lower temperatures.

2. The crystal structure of mercury-rich cadmium-mercury alloys was determined. The data obtained indicate a new rhombohedral solid solution terminal to pure mercury and a heterogeneous field separating the rhombohedral solid solution from the face-centered tetragonal previously discovered.

3. Heating and cooling curves were taken on the mercury-rich alloys and interpreted to indicate a peritectic reaction near the mercury ordinate of the constitutional diagram. The solid solution terminal to pure

mercury probably extends to 3.5 atomic per cent. cadmium, the hetero-
geneous field from 3.5 to 12 atomic per cent. cadmium, and the inter-
mediate solid solution field from 12 atomic per cent. cadmium to higher
concentrations in cadmium.

4. A new transition point was found in the intermediate solid solution
field. It is characterized only by a change in specific heat, not accom-
panied by any other thermal change and not accompanied by a change
in crystal structure.

ACKNOWLEDGMENT

The authors wish to acknowledge their indebtedness to Capt. E. G.
Oberlin, United States Navy, whose encouragement has made this work
possible.

DISCUSSION

L. W. McKEEHAN, New Haven, Conn.—My interest in this paper is partly
personal because it gives additional evidence for the correctness of the crystal struc-
ture for solid mercury proposed by Mr. Cioffi and myself[9] at a meeting of the American
Physical Society in Toronto, December, 1921. This rhombohedral arrangement
was, and still remains, unique, no other element being known to crystallize in the same
way. I must admit that the evidence on which we based our report now appears very
inadequate. The inadequacy was so patent to others that the compilers of the
International Critical Tables, in 1926, did not venture to decide between the structure
we described and the entirely different hexagonal structure described by Alsen and
Aminoff at about the same time.[10] Ewald and Hermann, in May, 1927, were still
more unkind, giving the preference to the hexagonal structure though this, too, was
unlike any other yet reported.[11] In the last two years, however, interest in solid
mercury has revived and more convincing evidence for the rhombohedral structure
has been published by Wolf[12] in Germany, by Terrey and Wright in England[13], and
now by Mehl and Barrett in this country. Lark-Horovitz[14] has also reported con-
firmatory results but has not given the data upon which they rest. The lattice dimen-
sions given by Mehl and Barrett agree exactly with those given by Terrey and Wright.
A tetragonal structure like that previously found by Mehl[15] for cadmium amalgams
between 23 and 50 per cent. cadmium, and now found to appear at as low as 10.4
per cent. cadmium, is also found by Terrey and Wright in copper amalgams. The
transition now found in the ω field of the cadmium-mercury phase diagram at from
−14° C. to −10.5° C. reminds one of the magnetic transformation in iron[16] and the
transition in β brass,[17] neither of which is accompanied by a change in crystal struc-

[9] L. W. McKeehan and P. P Cioffi. *Phys. Rev.* [2] (1922) **19**, 444–446.

[10] International Critical Tables (1926) **1**, 340.

[11] P. P. Ewald and C. Hermann: Strukturbericht 1913–1926, 42. [With *Ztsch. f. Kristallog* (1927) **65**, 3.]

[12] M. Wolf: *Ztsch. f. Phys.* (1929) **53**, 72–79.

[13] H. Terrey and C. M. Wright: *Phil. Mag.* [7] (1928) **6**, 1055–1069.

[14] K. Lark-Horovitz: *Phys. Rev.* [2] (1929) **33**, 121.

[15] R. F. Mehl: *Jnl.* Amer. Chem. Soc. (1928) **50**, 381–390.

[16] A. Westgren: *Jnl.* Iron and Steel Inst. (1921) **103**, 303–337.

[17] A. Phillips and L. W. Thelin: *Jnl.* Franklin Inst. (1927) **204**, 359–368.

ture, though a small change in lattice constant has recently been reported[18] to occur in the former case. In amalgams that give poorly defined patterns such changes are probably too small to be observed.

S. L. HOYT, Schenectady, N. Y.—This paper illustrates once again that many of the old diagrams which we have in our textbooks require revision when later work is taken up, especially when new methods of studying constitution are utilized. Such work requires a thorough mastery of the theoretical side of the question.

G. E. DOAN, Bethlehem, Pa.—This work of Dr. Mehl's has probably taken away from us the one remaining case of a system in which there is a peritectic transition and no other change. This was always a very useful example in teaching the peritectic reaction. Dr. Mehl, do you consider the change in the omega solid solution, in which there is no change in the lattice structure, of the same type as the change in beta iron that has aroused so much discussion recently? It is interesting to learn how there may be a great number of reactions in the solid state below room temperature, as this work, which was done around $-30°$ and $-40°$ C., shows, and probably a great number of our industrially important alloy systems would show changes of that kind upon investigation.

R. F. MEHL.—I deliberately avoided making any comparison of the omega transition in the cadmium-mercury system to the alpha-beta transition in iron or the beta-beta prime change in the copper-zinc system. Both of these last two changes involve no alteration in lattice symmetry and in this respect are similar to the omega transition in the cadmium-mercury system. But there appears to be no latent heat of transition in the omega transition, only a change specific heat, and in this respect the transition differs profoundly from the alpha-beta transition in iron.

It is, of course, entirely possible that low-temperature investigations should disclose new transitions in alloy systems already familiar at room temperature and above. But the viscosity (or, reciprocally, the atomic mobility if it is preferred to call it that) in alloys like the brasses, which solidify at temperatures of 800° or 900° C. must be very high (the atomic mobility low) at temperatures of $-50°$, and lower. The energy characteristics of the alloy at such a low temperature may require a transition, but the viscosity of the lattice may be so high as to restrain its occurrence. It is doubtful that a knowledge of such low-temperature transition would be of much practical value, but the scientific value might be considerable. Practically nothing has been done on this subject, so far as I am aware.

[18] R. Bach and A. Schidlof: *Compt. rend. de Genève* (1928) **45**, 151–154.

INDEX

591